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THE AMERICAN CHEMICAL SOCIETY.

XVIII.—Proceedings.

Regular Meeting, June 5, 1879.

The meeting was called to order at eight o'clock, Vice-President Leeds in the chair. The minutes of the last meeting were read and adopted.

Messrs. M. C. Nilson, J. Stillwell Schanck and Jas. H. Stebbins, Jr., were elected members.

It was, on motion, *resolved* that the names of the proposers and seconders of all candidates for membership be published in the minutes.

The Secretary stated that it was impossible to print the notification cards in proper time for the meetings, if the titles of papers were not sent in by their authors at least five days before the first Thursday of the month.

Prof. Morton read the first paper of the evening, entitled "Notes on the Chronology of the Isomeric Purpurines, and the Actual Relation of the Bodies which have been called by the names Anthrapurpurine, Isopurpurine and Flavopurpurine." He was followed by Mr. Bourgougnon, upon "Petroleum and its Examination;" and by Mr. Casamajor, on "A New Process for the Rapid Estimation of Pure Sugar in Raw and Refined Sugars."

Prof. Leeds then gave an abstract of his papers, entitled: I—"Solubility of Ozone in Water." II—"The Curious Discovery of the Reduction by Phosphorus, at Ordinary Temperature, of Carbonic Acid to Carbonic Oxide." III—"Bleaching by Ozone."

The Society then adjourned to the first Thursday in September.

S. A. GOLDSCHMIDT,
Recording Secretary.

XIX.—Notes on the Chronology of the Isomeric Purpurines and the Actual Relation of the Bodies which have been called by the names Anthrapurpurine, Isopurpurine and Flavopurpurine.

By HENRY MORTON, Ph.D.

There is a piece of recent chemical history which has already become somewhat involved on account of the oversight of some writers; and as the threads happen to be in my hands, I think I shall do a good office to future students by laying them out straight at the present time.

In 1870, Wm. H. Perkin published in the *Jour. of the Lond. Chemical Soc.*, a paper entitled, "On Artificial Alizarine" (volume viii, page 143), in which at the end, in a foot note, the author says: "When purifying artificial alizarine by converting it into an alumina lake, I found that upon digestion with carbonate of potash, this lake gave a red-colored solution, containing a coloring matter, dyeing mordants very similarly to alizarine, with this difference, that the reds are more scarlet, and the purples bluer, or more slaty. I have not obtained this body in a perfectly pure state as yet, but it appears to be crystalline."

The investigation thus opened by Perkin was diligently prosecuted by him, as appears from references to it in his other publications, and at the meeting of the London Chemical Society, held June 6th, 1872, he read a paper on this body, an abstract of which is published in the *Chemical News* for June 14th, and a fuller report of which appears in the *Journal of the London Chem. Soc.*, vol. xxv, p. 659, under the title "Note on a secondary coloring matter produced in the preparation of alizarine from anthracene." In these publications he gives the formula of the new body as $C_{14}H_8O_5$, and notes its relations and differences to and from the purpurine of madder. In the next volume of the proceedings, or rather *Journal of the Chem. Soc.*, viz., vol. xxvi, for 1873, p. 425, Perkin published under the title, "On anthrapurpurine," a long article on the same substance to which were attached, as illustrations, pieces of cloth dyed with it, as well as others dyed with alizarine.

This article has been translated and quoted extensively by other writers, but the others seem to have been overlooked or forgotten. Hence have arisen some of the errors which I now propose to correct.

From the above references it will be seen that Perkin first separated out and recognized this new body in 1870, and diligently

following up the research, published its formula in the beginning of June, 1872, and a full and exhaustive memoir in 1873.

In the *Moniteur Scientifique*, for August, 1872, or just two years after the first publication by Perkin, and just two months after the later one, in which he gave the formula of his new substance, appeared a communication announcing the discovery of a new product extracted from artificial alizarine, by G. Auerbach, and named by him isopurpurine. No mention whatever was made in this article of Perkin's prior publication, and it was, of course, generally inferred that Auerbach, who published a pamphlet on alizarine and its derivatives, in 1878, knew of them, but regarded his isopurpurine as a new discovery of his own and not a mere confirmation of Perkin's work. Moreover, a comparison of the properties of anthrapurpurine as given by Perkin, and isopurpurine as given by Auerbach, shows that two decidedly dissimilar materials were delineated by these two writers.

In the course of time it, however, appeared that Auerbach was ignorant of Perkin's prior publications, and, believing his material to be the same as that more fully described by Perkin, in 1873, claimed priority, insisting that his product and Perkin's were identical.

Into this error he seems to have led several writers; thus Græbe and Lieberman, in their report on artificial alizarine at the Vienna Exhibition, under the heading isopurpurine, refer first to Auerbach's publication in the *Moniteur Scientifique*, of August, 1872, and then to Perkin's third publication in the *Journal of the Chem. Soc.*, of 1873, omitting all reference to, and evidently not knowing of, his earlier publications in 1870, and June of 1872.

Rosenstiehl, in a recent article, has fallen into a like error, and credits Auerbach with first obtaining this body in an impure state, and Perkin with having first extracted it pure in 1873; but, admitting that Auerbach is right in assuming that what he extracted, was only the anthrapurpurine of Perkin, it is evident that he has no claim whatever to priority, but that the substance must be credited to Perkin, and must be called by his name of anthrapurpurine.

As a matter of fact, however, the substance actually extracted by following the method described by Auerbach, in 1872, was not anthrapurpurine, but a mixture consisting mainly of a substance which was new at that time, but was afterwards isolated by Messrs. Schunck and Roemer; and, that if Auerbach had not unfortunately overlooked Perkin's prior claims, and sought to identify his isopur-

purine with Perkin's anthrapurpurine, he would have been the first discoverer of flavopurpurine, in place of Schunck and Roemer.

My reasons for this opinion are the following: In the latter part of 1874, I had occasion, together with my friend, Mr. Wm. E. Geyer, B. S., to repeat both Perkin's and Auerbach's methods of treatment upon considerable quantities of artificial alizarine.

We first followed out Perkin's method, and obtained a product corresponding in all respects with his description of anthrapurpurine.

We then worked on another quantity of artificial alizarine, according to Auerbach's directions, and when we came to the last treatment, namely, solution in, and crystallization from, alcohol, we found that we evidently had to do with a mixture of two bodies, differing in a marked way as to their solubilities.

Bearing in mind that we had found Perkin's anthrapurpurine as he describes it, but little soluble in alcohol, and that Auerbach described his isopurpurine as quite soluble, we so carried on the alcohol treatment as to reserve the soluble part as isopurpurine, and reject the less soluble portion.

When we had carried this separation to a sufficient extent, we found that we had a body entirely distinct from Perkin's anthrapurpurine, but sufficiently like the description given by Auerbach of his isopurpurine, to answer for it, when due allowance was made for the uncertainties of a verbal description.

When, however, the paper of Schunck and Roemer appeared in 1876, we saw that the body we had extracted agreed still more closely with their flavopurpurine. Having obtained it, however, by the process described in 1872, by Auerbach, I continued to call it by his name, and should do so still had he not very emphatically repudiated all credit for and connection with it subsequently to his first publication and description.

I am now inclined to think that, subsequently to his first publication, Auerbach so modified his alcohol treatment (being desirous to show identity with Perkin's anthrapurpurine), as to collect the less soluble portions, and thus threw away the new discovery within his reach, in his effort to secure that which belonged to another.

In fact, a careful comparison of the description which Auerbach published in 1872, of his isopurpurine, with the known properties of anthrapurpurine, show conclusively that the body described by Auerbach could not possibly have been, even in large part, anthrapurpurine, but must have been essentially flavopurpurine, with a small amount of anthrapurpurine mixed with it.

Thus, he says, that it dissolves in ammonia with a brownish-red, and in alkaline carbonates, with a color equally red, with a very marked brownish shade. Now, pure anthrapurpurine gives purplish-red solutions with both of these solvents, while flavopurpurine gives solutions of an orange-red color, very marked. A mixture would produce the brownish shade named by Auerbach. Again, on the iron mordant, Auerbach says his isopurpurine gives a brownish-violet, which is exactly what flavopurpurine does, while pure anthrapurpurine gives a slaty-blue, as noticed by Perkin, and which is very manifest even when an impure specimen is used. So on with his other tests or properties.

The true relation of the substances which have borne the names given at the head of this article, is, then, this:

Anthrapurpurine is a single substance, first isolated by Perkin, partially in 1870, and thoroughly prior to June 6th, 1872.

Isopurpurine, as described by Auerbach, in 1872, is a mixture, in proportions varying according to the composition of the artificial alizarine, from which it is extracted, and the way in which the alcoholic treatment is conducted, of anthra- and flavopurpurine, with a trace of alizarine. This mixture was first separated and described by G. Auerbach, in the *Moniteur Scientifique*, for August, 1872.

Flavopurpurine is a single substance or chemical individual, first separated, as a matter of fact, by Mr. Geyer and myself, but not then published by us, and thus first isolated and described by Schunck and Roemer, in the Berichte d. d. chem. Gesellsch., 1876, p. 678.

The facts, as to the composition of the material obtained by treating artificial alizarine by the method described by Auerbach, are also established by the recent researches of M. A. Rosenstiehl, presented to the Chemical Society of Paris, and published in the bulletin of that body, of May 5th and 20th, 1878, where in vol. xxix, p. 408, I find as follows: "On submitting isopurpurine obtained by the method described by Mr. Auerbach, to proximate analysis, I was not slow in discovering the presence of about 15 p. c. of alizarine." Here follows a long and minute description of how this was removed by treatment with hot benzol. The material so purified was then dissolved in boiling alcohol, and allowed to deposit crystals on cooling. The author then continues:

"Comparative dyeing tests made with the part crystallizing out and with that remaining in the mother liquor, showed that the alcohol eliminated a substance coloring mordants like flavopurpurine, that is to say, of a red more orange than that of oxanthraflavone."

It should be mentioned, that in this essay its author indicates by the word oxyanthraflavone the material isolated by Perkin's method, but which, through oversight of the earlier publications, he credits to Auerbach, and names isopurpurine in consequence of this mistake. We have recently repeated, with a portion of the flavopurpurine separated by us in 1875, by repeated solutions in alcohol, all the tests given by Schunck and Roemer, including the examination of its absorption spectrum, and these tests show it to have been perfectly pure flavopurpurine.

The swatches of dyed test cloth accompanying this paper, as illustrations, speak for themselves. The peculiar slaty-blue of the iron mordant noticed by Perkin, is strongly contrasted with the "brownish-violet" of the corresponding part of the swatch dyed with flavopurpurine. The characteristic differences elsewhere are also readily seen. The materials with which these swatches are dyed, are essentially pure, or as pure as it was practicable to make so large a quantity as was required within a moderate time.

STEVENS INSTITUTE OF TECHNOLOGY, HOBOKEN, N. J.

XX.—PETROLEUM AND ITS EXAMINATION.

BY A. BOURGOUGNON.

Received June 9, 1879.

In this communication to the American Chemical Society, I will describe the mode of examination which I have adopted in examining the different kinds of petroleum and its products. This method of analysis is the result of several years' experiments.

Before entering directly upon my subject, I think that a brief description of the general process employed in obtaining crude oil will be acceptable, and I will therefore relate some observations made during a recent trip through the oil-bearing territory.

I here take occasion to tender my thanks to Mr. J. Labouret, for his valuable information, and to A. J. Pouch, Esq., of the firm of J. A. Bostwick & Co., who has favored me with several samples very useful in my investigations.

Petroleum is found in several parts of the world, but the most abundant field of production is situated in Pennsylvania. It is also met with in several other States of the Union, but the Pennsylvania oil is justly considered the best in quality for illuminating purposes.

Contrarily to the rule governing the occurrence of most mineral substances, which are confined to well determined geological forma-

tions, petroleum occurs in rocks of nearly all ages, from the Lower Silurian up ; most abundantly in shales and sandstones ; also, to some extent, in limestones. In the Rangoon and Caspian regions, the oil occurs near the surface in clayey soil, and collects in shallow pits. A noted locality is Ye-nan-gyoung, in Burmah, where the wells are narrow shafts, 180 to 300 feet deep, and large enough for a man to work in. In Persia, the oil is largely found at Baku, on the west shore of the Caspian ; China yields a small amount of oil ; Japan has small and undeveloped districts ; New Zealand, also, shows indications. In the Caucasus, Russia, surface wells have long been worked, and lately wells have been sunk with success. In Gallicia, Austria, are wells yielding largely ; and Alsace and Hanover have produced some oil. Petroleum has likewise been found in Peru, Ecuador, Southern Mexico, San Domingo, Trinidad and Nova Scotia, in small quantities. In Canada, petroleum occurs mainly in the corniferous limestone of the Lower Devonian, but is also found in greater or less quantity in the bird's-eye limestone of the Lower Silurian, and the Lower Helderberg limestone of the Upper Silurian.

In the United States, oil is very abundant in Western Pennsylvania, and has been found in considerable quantity in West Virginia, Ohio, Kentucky and Tennessee. It has also been found in New York State, in Michigan, Indiana, Colorado and California. The oil of Southern California comes from tertiary shales. The upper oil-region of Pennsylvania begins in the vicinity of Tidioute, on the Alleghany, in Warren Co., and runs southwest of Titusville, thence nearly south, along Oil Creek, into Venango Co., to Oil City, and thence southwest to Franklin.

The lower oil belt begins at Triangle City, Beaver Creek, Clarion Co., and runs southwest twenty-one miles to St. Joe, in Butler Co. In 1866, rock with some oil was struck at Brady's Bend, at a depth of 1,100 feet, giving rise to further investigation of the river above, which resulted in the discovery of a sand rock of 57 feet thickness at a depth of 960 feet, on the Alleghany River at Parker's Landing. The oil-bearing rock of Pennsylvania is a sand-rock, of which different strata are struck at different depths.

Various opinions have been advanced upon the origin of the formation of petroleum. It was almost generally admitted that petroleum was derived from vegetable or animal matter. Another explanation was that petroleum was of a similar formation to coal, but under a different condensation. Amongst the more recent explanations upon the formation of petroleum, it has been suggested

that this hydrocarbon was produced by natural distillation of coals and bituminous shales. Lesquereux attributes its origin to the partial decomposition of low form of marine vegetation, while Berthelot has advanced the theory that by complex chemical changes at present taking place in the interior of the earth, petroleum is continually set free.

Petroleum has been known for ages. The spring of Zante, one of the Ionian Islands, was mentioned by Herodotus more than two thousand years ago; and Pliny says that the oil of a spring at Agrigentum, Sicily, was used in lamps. The city of Genoa was formerly lighted from the wells of Amiano, in Parma, Italy.

Prof. A. E. Foote (AM. CHEM., Nov., 1872) states that Peter Kahn, in his *Travels in North America*, published in 1772, gives a map of the Pennsylvania oil springs in 1771; but, according to H. E. Wringley, the earliest mention of petroleum in that State occurred in the report of the commander of Fort Duquesne, 1750, when he witnessed the ceremonies of the Seneca Indians on Oil Creek. A prominent feature of the ceremonies was the burning of the oil as it oozed from the ground.

In 1819, Dr. S. P. Hildreth, in the *American Journal of Science*, alluded to the discovery of petroleum in Ohio, on the little Muskingum River, and wrote: "It is beginning to be in demand for lamps in workshops and manufactories. It affords a clear, bright light when burnt in this way, and will be a valuable article for lighting the street lamps in the future cities of Ohio."

The oil spring of Cuba, Alleghany Co., N. Y., called the Seneca Oil Spring, was described by B. Silliman, in 1833, as a dirty pool, about 18 feet in diameter, covered with a film of oil, which was skimmed off from time to time for medicinal purposes.

In 1854, the Rock-oil Company was formed for the purpose of gathering oil in the vicinity of Oil Creek. The process employed by this company was to collect all the surface oil they could by means of cloths, which were subsequently squeezed into tanks. In 1858, Col. E. L. Drake, the superintendent of the Rock-oil Co., conceived the idea of boring an artesian well near Oil Creek. After several experiments conducted with the persistency and enthusiasm of discoverers, he, at last, in 1859, struck oil. A wild excitement prevailed throughout the country and almost every body was stricken with the "oil fever;" companies were formed to bore for petroleum, and in New York alone, 317 of these companies were formed, representing a capital of more than two hundred millions of dollars.

Petroleum is extracted from bored wells of a variable depth, and about 7 inches diameter. Wells can be classified as follows: Flowing wells, pumping wells, gas wells, salt-water wells and dry holes.

The commercial history of petroleum begins with the Drake well, bored in 1859, near Titusville. At a depth of 60 feet only, oil was struck, and the daily production was 25 barrels.

The first flowing well was situated on the McEllenny or Funk farm. Oil flowed in June, 1861, at the rate of 250 barrels a day for fifteen months and then stopped. Other flowing wells were bored, and amongst them the following are remembered: The Phillips well, on the Tar farm, with a daily production of 2,000 barrels; the Empire well, daily production 4,000 barrels for nearly a year, and then dropped to a pumping well, yielding 100 barrels a day; the Sherman well flowed 1,500 barrels daily for several months, when it declined to 700 barrels, and continued flowing for twenty-three months; the Coquette, well known as the "glory of the oil region," manifested a surprising peculiarity—after flowing 600 barrels a day for several months, it suddenly increased its yield with great rapidity, and reached 2,000 barrels per day.

Flowing wells, like the above, are not now to be found through the oil region, but intermittent wells are sometimes bored. They flow at regular intervals, between which they are pumped.

Pumping wells are worked by steam engines, and the crude oil is received in a wooden tank. When this tank is full, it is gauged, and its contents are transferred by means of iron pipes into large iron tanks. These large tanks are the property of the pipe companies, who buy all the production of the country. From their tanks the pipe companies send the oil to their stations on the railroads through iron pipes, 2 or 3 inches in diameter, and from these stations petroleum is delivered into iron cars of a cylindrical form, holding about 85 barrels.

Throughout the oil district, 42 gallons are equivalent to 1 barrel, but the pipe companies take 43 gallons for the barrel, this extra gallon covering their charges for removing the oil from the tanks of the producer into their own.

The market oil delivered for a cargo is, therefore, not produced from a single well, but is the production of a whole district. Before the establishment of the pipe companies, the producers were obliged to send the oil to the railroad stations; now they are relieved of their trouble, since the pipe companies take oil directly from their wells, and pay for it prices fixed at the Petroleum Exchanges. Wells are bored by contract for so much a foot, but there is no external indi-

cation to prefer one place to another, although experiment has shown that the petroliferous zone follows a line having an inclination of 22° from north to south. This indication is not always correct, since producing wells have been bored out of the 22° line, some time as far as 16° inclination, and other wells bored in the neighborhood, or even upon the 22° line, have proved to be dry holes. The yield of a well decreases sometimes very rapidly, and the general belief is that the well is obstructed by solid hydrocarbons, such as paraffine. In order to remove this obstruction, a torpedo of dynamite is generally exploded in the well, which is intended to break the walls of the natural petroleum reservoir, thus connecting the shaft with it. The cost of such a torpedo is very high, and some producers try to dissolve the solid hydrocarbons by means of benzine. About 50 barrels of benzine are poured into the well, and after a lapse of twelve hours they are removed by pumping. In several instances, the benzine only dissolved paraffine, and the produce pumped as crude oil was merely a solution of paraffine in benzine. The use of the torpedo is not always followed by success. I was shown a well at Summit,the daily production of which had been 60 barrels, but its owner not being satisfied (a neighboring well yielding 100 barrels daily), resolved to have a torpedo exploded in his well. The result was that the daily production was reduced to 16 barrels. The average depth of producing wells is about 1,200 feet, and petroleum is designated under the name of third or fourth sand, according to the stratum where it comes from. This denomination is derived from the fact that before reaching the rocks bearing oil, the following layers are to be bored. 1st—The earth surface ; 2d—First layers of slate rock ; 3d—First sand rock ; 4th—Second slate rock ; 5th—Second sand rock ; 6th—Third slate rock ; 7th—Third sand rock ; 8th—Fourth slate rock ; 9th—Fourth sand rock. The color of the third sand oil is darker than that of the fourth, and the specific gravity heavier by about one degree Baumé. At Butler, crude oil is amber colored, and comes from the fourth sand. The cost of a derrick and the boring of a well is about twelve hundred dollars.

In these last years, the oil known under the name of Parker's oil has been in general demand abroad, as furnishing, when refined, a better quality burning oil than other crude oils. The fact, however, is, that other oils may yield just as good products as Parker's oil, but their treatment is more expensive.

It is estimated that the Parker District covers about 750 square miles.

Parker's oil is pumped to the following stations:

Harrisville,	Monterey Station,
Fullerton Station,	Sarah Furnace,
Foxburg "	Brady's Bend,
Parker "	Sligo.

Parker's oil is generally clear. At Butler, it is amber colored, but the color is darker in Millerstown; darker yet in Petrolia, Karns and Parker; and the oil from Foxburg has no longer the reddish tinge of the oil from the above-mentioned localities.

Although the denomination of Parker's Landing oil is generally adopted, we must remark that in the revised rules of the N. Y. Produce Exchange, the word Parker does not appear; it is, however, understood that when a contract calls for Parker's oil, the oil delivered must be of the first quality.

The examination of American petroleum by Pelouze and Cahours has established the existence of a series of hydrocarbons homologous to marsh-gas. All these hydrocarbons are acted upon by chlorine, which produces a successive elimination of hydrogen, under the form of hydrochloric acid, and the substitution of an equivalent quantity of chlorine. The first term of the substitution for each of these hydrocarbons, is represented by the chlorhydric ether of the corresponding alcohol. All these chlorhydric ethers, heated with sodium, give sodium chloride and an hydrocarbon, containing two atoms less of hydrogen than the primitive hydrocarbon, thus converting the original marsh-gas series into the corresponding olefines. The hydrocarbons isolated and studied by Pelouze and Cahours are the following:

HYDROCARBONS.	FORMULA.	BOILING POINT.	SPECIFIC GRAVITY.	
			LIQUID.	VAPOR.
Butyl hydride....	C_4H_{10}	0°C.	0.600	
Amyl "	C_5H_{12}	30°	0.628	2.557
Caproyl "	C_6H_{14}	68°	0.669	3.055
Oenanthyl " ...	C_7H_{16}	92°–94°	0.699	3.600
Capryl "	C_8H_{18}	116°–118°	0.726	4.010
Pelargyl "	C_9H_{20}	136°–138°	0.741	4.541
Rutyl "	$C_{10}H_{22}$	158°–162°	0.757	5.040
Undecyl "	$C_{11}H_{24}$	180°–182°	0.766	5.458
Lauryl "	$C_{12}H_{25}$	198°–200°	0.778	5.972
Conicyl "	$C_{13}H_{28}$	218°–220°	0.796	6.569
Myristyl "	$C_{14}H_{30}$	236°–240°	0.809	7.019
Benyl "	$C_{15}H_{32}$	258°–262°	0.825	7.526
Palmityl "	$C_{16}H_{34}$	280°		8.078

It seems probable, that, when petroleum is dissociated by heat, the products of the distillation must belong to another series than the marsh-gas. I have already begun the examination of the products of dissociation of petroleum, and I hope I will be able, before long, to bring my results before the American Chemical Society. For the present I will only state that I have observed the phenomena of fluorescence in several liquid hydrocarbons, resulting from the destructive distillation of petroleum.

I let here follow a table containing valuable information about petroleum from different localities, taken from A. Wurtz's *Dictionnaire de Chimie* :

Origin.	Heavy oil Virginia	Light oil Pennsylvania.	Heavy oil Penn.	Parma.	Java.	Pechelleon.	Gabian.	Hanover.	Gallicia.	Circassia.	Berniania	China.	Caucasus.	Heavy oil of coal.
Volatile products at 100°C.	1.0	4.3	.....	1.1	1.0	.....	.....	0.5	2.1	3.3	.....	.....	.. ....	.....
" 140°	1.3	16.0	.....	33.3	.....	.....	.....	5.0	8.7	15.7	4.9	1.0	2.7	.....
" 180°	12.0	28.7	.....	60.5	7.7	7.8	.....	... ...	14.3	24.0	5.8	20.0	13.3	. .....
" 200°	. ....	31.0	.... .	69.3	15.0	15.2	.....	11.0	21.7	27.7	... ...	35.0	.....	12.5
" 220°	... ..	... ..	.....	.....	22.3	25.7	.....	14.0	25.3	32.7	8.0	45.0	19.0	.....
" 260°	.....	.....	....	.....	30.0	40.6	.....	20.0	33.0	35.0	14.0	70.0	29.3	.....
" 280°	.....	.....	12.0	.....	... ...	. .....	0.5	.....	... ...	.....	.....	.....	36.0	.....
Specific gravity at 0°C.	0.873	0.816	0.886	0.786	0.923	0.892	0.894	0.892	0.870	0.887	.....	0.680	0.884	1.044
" 50°C.	0.853	0.784	0.853	0.747	0.888	0.857	0.831	0.860	0.836	0.850	.....	0.622	0.854	1.007
Co-efficient of expansion	0.00072	0.00084	0.00072	0.00106	0.000769	0.000793	0.000867	0.000772	0.000813	0.000750	0.000774	0.000824	0.000724	0.000743
Composition — Carbon	85.3	82.0	84.9	84.0	86.2	85.7	86.1	80.4	82.2	84.2	83.8	83.5	86.3	82.0
Composition — Hydrogen	13.9	14.8	13.7	13.4	12.2	12.0	12.7	12.7	12.1	12.4	12.7	12.9	13.6	7.6
Composition — Oxygen	0.8	3.2	1.4	1.8	1.6	2.3	1.2	6.9	5.7	3.4	3.5	3.6	0.1	10.4
Heat of Combustion	10180	9963	10072	10121	10831	10020	.....	.....	10005	.... ..	.....	.... ..	11460	8916

Important information is derived from this table, as it furnishes the coefficient of expansion of petroleum, and the knowledge of this coefficient determines the empty space which must be allowed in the vessel containing the oil. This space will be :

$$V. K. 50.$$

V represents the volume of the oil ; K, the coefficient of expansion ; and, at the same time, we base our calculation on the assumption that the oil is to be submitted to a change of temperature of 50° C.

The coefficient of expansion of Pennsylvania crude oil varies from 0.00072 to 0.00086, according to the amount of naphtha contained in the oil. These coefficients, therefore, bear a certain relation to the gravity of the crude oil, and for the products of distillation the following numbers can be generally adopted with satisfactory results :

Under 0.700,	gravity at 15° C.	=	0.00090
Above 0.700 to 0.750,	" "	=	0.00085
" 0.750 " 0.800,	" "	=	0.00080
" 0.800 " 0.815,	" "	=	0.00070
" 0.815,	" "	=	0.00065

In the above table of Wurtz, the numbers representing the percentage of oxygen in the composition of petroleum, are apparently too large, since the fact that crude oil generally contains sulphur is not taken into consideration. In Canada oil the amount of sulphur is large, but in Pennsylvania petroleum I have detected only traces of this substance.

PETROLEUM OR CRUDE OIL.

Petroleum has been classified as follows, according to quality :

First Class. The production of Butler, Clarion, Armstrong and Venango Counties, Pennsylvania (excepting Bullion District).

Second Class. The production of Warren, Tidioute, Fagundas and Garland Districts, Pennsylvania.

Third Class. The production of Bullion District, of Venango County, the Bradford District, of McKean County, Pennsylvania, and the Limestone District, of Cattaraugus County, New York.

Inspectors appointed to examine petroleum, must employ all the means they possess for the determination whether an oil really is within the contract of sale.

A *fractional distillation in ten parts* is generally considered an examination of petroleum. This process is short, but the results are far from being satisfactory, and it is for this reason that we have entirely rejected it, and have adopted instead the *fractional distillation in one hundred parts.* The advantages gained are the following: 1. Exact determination in volumes and weights of the different products, as naphtha, benzine, burning oil and residuum. 2. The determination of the presence of paraffine oil as soon as it appears in the products of distillation. Paraffine oil is always present in the distillate when the first products of decomposition are observed.

When petroleum is heated, one part of it will distill, and if the distillation is fractioned into one hundred parts, the specific gravity of each hundredth is always increasing until the hydrocarbons remaining in the retort reach a temperature at which they cannot exist; at this moment, therefore, decomposition occurs, and the result is a deposit of carbon and paraffine in the retort; also, gases escape, and a decrease in the specific gravity of the distilled liquid is observed.

This phenomenon of decomposition can be explained in the following way: According to the hypothesis of R. Pictet, temperature is the measure of the amplitude of calorific motion, *i.e.*, the amplitude of motion increases directly with the temperature. At first, the amplitude of motion produces merely distillation; but, in continuing the distillation, a point is reached where the hydrocarbons remaining in the retort reach a temperature at which they cannot exist without undergoing a partial decomposition, although this temperature is not high enough to produce ebullition. In short, the hydrocarbons $C_{2n}H_{2n+2}$, are decomposed before reaching their point of ebullition. The products of decomposition are substances of lower gravity and boiling point; therefore, instead of an increase, a decrease of specific gravity, as well as temperature, is observed. The decrease in the temperature also shows that the dissociation has been accompanied by an absorption of heat.

The point where dissociation occurs during the distillation of petroleum, is of importance for the refiner, for, from this point until the end of the distillation, paraffine is deposited in the retort, and the last portions of the distillation give only paraffine oil, which is not fit for illuminating purposes. Burning oil need not, however, be entirely free from paraffine. It is, to the contrary, in the interest of the refiner to employ as much as he can of this product, but he must

always bear in mind that paraffine oil decreases the illuminating power of the burning oil.

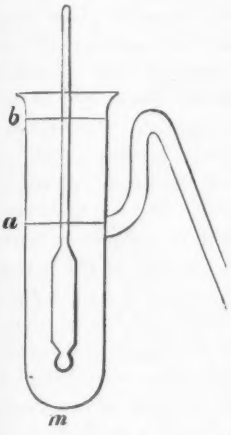
During the distillation, a thermometer must be placed in the retort to show at any moment the temperature of the vapors, as this observation of temperature is very important. A certain relation exists between the temperature at which a product distills and its specific gravity. When a sample of pure petroleum is distilled in one hundred parts, the temperature at which each hundredth distills follows an arithmetical progression, as also do the densities of each hundredth. The temperature, when distillation commences, varies; but, with an increase of 2° C., we also note an increase of specific gravity of $\frac{3}{1000}$. This increase of temperature and specific gravity begins only, when the lighter products have distilled, and ceases with the appearance of the first products of decomposition.

One of the greatest advantages of the fractional distillation in one hundred parts, is a positive knowledge acquired upon the purity of the sample submitted to examination. If, during the distillation, before the appearance of the products of destructive distillation, when the temperature has reached about 320° C., the distillation is stopped, the specific gravity of the remaining oil in the retort must agree with its theoretical specific gravity. If, between the observed specific gravity and the theoretical specific gravity, there should exist a noted difference, and, on the other hand, if, during the first part of the distillation, the densities and temperatures had not followed a regular progression, the conclusion is, that the petroleum under examination is not pure and will interfere seriously with the interest of the refiner. I should observe, however, that even for a pure sample of petroleum, the theoretical and observed specific gravities always differ slightly, since, during the first part of the distillation, a certain amount of uncondensable gas escapes and cannot be taken into consideration for the calculation of the theoretical specific gravity.

During the distillation, the appearance of the distillate must be carefully noted, the most important being the color of the products distilled, and also the temperature when paraffine oil commences to solidify, by cooling with cold water. But not only the point of solidification need be observed, but also the temperature at which the oil loses its transparency. The fluorescent appearance of the distillates should likewise be noted. The last products of distillation show generally a blue fluorescence; should, however, a green fluorescence be observed, the sample of petroleum is suspicious, as I ob-

served that this is found in petroleum to which residuum of former distillation had been added.

In order to save time during the distillation, I use the following apparatus, in which the product of the whole distillation is allowed to pass into or through the same vessel. This glass vessel contains exactly 20 cc from m to a and 10 cc from a to b; this part is connected with a syphon of a special form, which, when in action, each time removes 10 cc, or 1 volume. $a\ m$ is filled with two volumes, having a density, d, giving a weight, $2d$. 1 volume, or 10 cc, is received from the worm, having a weight or density, δ_1, which is found from the whole specific gravity, D, by the use of the following calculation. The glass contains $2d + \delta_1$, having a density $\frac{2d + \delta_1}{3} = D$.



The density, D, is given by a densimeter plunging in the glass vessel. The density, δ_1, is evidently $\delta_1 = 3D - 2d$; it remains in the glass, 2 volumes having a weight, 2D; another volume, δ_2, is received, and when the syphon is filled it contains 3 volumes, having a density $\frac{2D + \delta_2}{3} = D_1$, whence $\delta_2 = 3D_1 - 2D$. The densities, $\delta_3 \delta_4 - \delta_n$, are obtained in the same way. The syphon discharges the liquid in a vessel containing a densimeter, indicating the specific gravity of the distillate. For a receiver divided in 10 cc, as described above, the quantity of petroleum to be distilled is 1 kilogramme.

An analysis of petroleum, conducted as above described, is not yet complete for the purposes of a refiner, it being necessary to add a lamp assay to determine the hourly consumption, and a photometric assay to determine the illuminating power of the burning oil. In order to make these two determinations, the distillate forming the burning oil is refined, as in the factories, by means of sulphuric acid, caustic soda and washing with cold water. When the water is separated from the oil, it is now ready for the determination of its flashing and burning point, and also for the lamp and photometric assay. The results of the analysis may be tabulated, as we have done in a former communication to the American Chemical Society, but it is more convenient to adopt a graphical method to represent the re-

sults. Upon the line of the abscisses the volumes are inscribed, and on the ordinates the specific gravities and corresponding temperatures, from which the curve of temperature and the curve of specific gravity are obtained.

Before distilling the sample of petroleum, it must be submitted to preliminary examinations; the first thing to ascertain is its specific gravity; the color and smell are noted. A thin layer of about two millimeter thickness is poured on a plate and left undisturbed for twelve hours, when it must not have any trace of soft or solid matter, but must remain fluid. A small quantity, about 100 cc, of the sample is placed in a platinum dish and ignited. Pure petroleum treated in this way will burn almost entirely, leaving a residue having a weight not exceeding 1 per cent. of the crude oil used. This residue is composed partly of oxide of iron. Before, however, weighing the platinum dish, it must be heated to completely burn the carbon deposited on its sides during the burning of the petroleum. For the distillation of petroleum I have adopted a copper retort, holding $2\frac{1}{2}$ liters. A glass retort can be employed, but as crude oil contains generally some water, the glass is in danger, and severe accidents may result. It has been claimed that a glass retort offered the advantage that the distillation of paraffine oil could be observed. This assertion I doubt, and maintain that to make a distillation of petroleum in a copper still furnished with a thermometer, is more accurate to indicate the presence of paraffine oil, and is, at the same time, perfectly safe for the operator.

NAPHTHA.

In The Proceedings of the American Chemical Society, Vol. I, p. 119, I have described a process for the determination of naphtha in crude oil. Two kinds of naphtha are in the market: crude naphtha or "distillate," and deodorized naphtha. Deodorized naphtha is generally asked for. Naphtha shall be colorless and sweet (deodorized), and of gravity of from 68° to 73° Baumé.

Naphtha must not contain any oil; placed upon white paper, it must entirely evaporate, without leaving any greasy stain. A small quantity rubbed between the hands must evaporate quickly and leave the hands dry. To see if naphtha has been well washed, a small quantity is treated by diluted sulphuric acid in a bottle, and agitated; the acid and naphtha must remain colorless. If naphtha of a very light gravity, is asked for, it is important to ascertain that it does not contain relatively heavy products; the only way to prove

this is distillation, where, however, only the specific gravities of the last products are observed.

REFINED PETROLEUM.

According to the rules regulating the petroleum trade, refined petroleum shall be standard white, or better, with a fire test of 110° Fahrenheit, or upwards. After having verified these points, the inspector must satisfy himself that the oil is not acid, and does not contain too large a proportion of heavy oil.

Recently complaints were received from Germany about the quality of the kerosene received. It was stated that the burning oil received at Bremen was not well refined, and was often acid. During the discussion of the reclamations of the German merchants, it has been advanced that kerosene could not be acid, for if sulphuric acid had been present, the kerosene should have shown a dark color.

That sulphuric acid produces a dark color with burning oil, is a well-known fact; but it must be remembered that in the action of sulphuric acid upon kerosene, when the sludge acid is produced, sulphuric acid is decomposed and produces sulphurous acid. Besides, the acid used for refining is not chemically pure, and generally contains oxides of nitrogen. From these remarks it follows, that if sulphuric acid is not present in burning oil, this substance may contain either sulphurous acid or oxides of nitrogen, if the acid treatment has not been followed by washing with alkalie, and finally water.

To examine for these acids, we treat the kerosene with an alcoholic solution of caustic soda. After separating this solution, it is evaporated, and the residue examined.

To ascertain if the kerosene contains too large proportions of heavy or paraffine oil, it is cooled down and the temperature at which the paraffine begins to solidify, is observed. It is evident that kerosene must remain fluid at the winter temperature of the place where it is stored.

A very good way of ascertaining if kerosene has been well refined, is to submit it to a photometric assay.

First, a sample of about two liters is obtained and divided into two parts. The first sample is submitted to the lamp assay and to the photometric assay, then the second sample is refined by treatment with sulphuric acid, caustic soda and water. If the result given by the photometric assay of the second sample corresponds with the result obtained by the first sample, the kerosene examined was well refined. Heavy oils in kerosene decrease its illuminating power. If a sample of kerosene, after being well refined, has an il-

luminating power below a standard admitted, it will be safe to conclude that the decrease of brilliancy in the light is due to the presence of heavy oils. If, during the lamp assay, which furnishes the hourly consumption of kerosene and enables us to compare the price of kerosene with the price of other kinds of lights, the wick of the lamp gives off fumes and turns black by carbonization during the burning of the last parts of oil, this is an indication that the kerosene was not well refined, and was, perhaps, acid.

I have lately examined several samples of kerosene of the largest refineries of New York, and I did not meet with a single sample containing acids. The process of washing kerosene with water and testing the washings with litmus paper, must not be relied upon, as often blue litmus paper is too alkaline to indicate small quantities of acid.

Kerosene must stand a fire test of 110° Fahrenheit. It has been often pointed out, that the fire test of kerosene is of little importance, for the real danger in the handling of oil is at the point where it gives off an explosive vapor. The French law requires that kerosene must not give off an inflammable vapor at a temperature of 35° C.

Several kinds of apparatus have been devised for the determination of the flash test and fire test of burning oil. The most reliable is an open vessel containing the oil to be tested; the inflammation is produced by an electric spark.

RESIDUUM.

The residuum must be free from coke, liquid at ordinary temperature, and must not contain any burning oil. In foreign countries the residue is free of duty, provided it does not contain any burning oil, otherwise the duty will be the same as for crude oil. The instrument used in America for ascertaining the gravity of petroleum and its products, is the hydrominor areometer of Baumé. On the continent densimeters are generally substituted, and very often discussions arise about the gravity of petroleum, for the tables comparing degrees Baumé and the density are not alike. I think that the areometer of Baumé must not be entirely discarded, because the numbers indicating the gravity are smaller and more readily remembered than the numbers given by the densimeter. The construction of the densimeter is far more difficult than that of the hydrometer; their stems may be divided as to indicate specific gravities directly; for this purpose, if we denote by w the weight

of the densimeter, by v the volume of the liquid displaced, and by d its density, we shall have

$$w = d.\ v,$$

as the equation which will enable us to calculate the volume displaced for any corresponding density, and allow us to graduate the stem accordingly. This equation is that of the hyperbola; if, therefore, the specific gravities be supposed to vary by equal differences, the corresponding volumes will vary unequally, or the stem must not be divided into equal parts, but into intervals proportionate to the difference of consecutive ordinates of the hyperbola. Such densimeters are consequently of rather difficult construction, and require skill and intelligence on the part of the manufacturer. In a former communication to the American Chemical Society, I have given the formula to be employed to transform the degrees of Baumé's hydrominor areometer into corresponding specific gravities (Proceedings of the American Chemical Society, Vol. I, p. 45).

The formula referred to is

$$\frac{144{,}329}{134{,}329 + N} = D,$$

in which N = degree Baumé, and D = sp. gr.

N	D	N	D	N	D	N	D	N	D
10	1.000	24	.911	38	.837	52	.774	66	.720
11	0.993	25	.905	39	.832	53	.770	67	.716
12	.986	26	.900	40	.827	54	.766	68	.713
13	.979	27	.894	41	.823	55	.762	69	.709
14	.973	28	.889	42	.818	56	.758	70	.706
15	.966	29	.883	43	.813	57	.754	71	.702
16	.960	30	.878	44	.809	58	.750	72	.699
17	.953	31	.872	45	.804	59	.746	73	.696
18	.947	32	.867	46	.800	60	.742	74	.692
19	.941	33	.862	47	.795	61	.738	75	.689
20	.935	34	.857	48	.791	62	.735	76	.686
21	.929	35	.852	49	.787	63	.731	77	.682
22	.923	36	.847	50	.783	64	.727	78	.679
23	.917	37	.842	51	.778	65	.724	79	.676

Volume of the areometer at + 15°C. = 144,329.

A fractional distillation of a sample of petroleum, taken by myself, from a well at Millerstown, Pa., gave the following results.

This well, called the "Great Leather," is 1430 feet deep; once in an hour it flows during ten minutes, and is then pumped. Daily production 200 barrels. Temperature of the oil taken directly from the well = 10° C., specific gravity at + 15° C. = 0.790.

DISTILLATION.

	Gravity.		Gravity.		Gravity.				Gravity.
1	.662	21	.730	41	.768	61	.807	81	.807
2	.665	22	.733	42	.770	62	.809	82	.812
3	.668	23	.735	43	.772	63	.810	83	.812
4	.670	24	.737	44	.774	64	.812	84	.812
5	.676	25	.739	45	.775	65	.815	85	.813
6	.681	26	.741	46	.777	66	.817	86	.811
7	.686	27	.744	47	.779	67	.817	87	.810
8	.690	28	.746	48	.782	68	.814	88	.809
9	.695	29	.748	49	.784	69	.819	89	.809
10	.699	30	.749	50	.787	70	.822	90	.810
11	.703	31	.750	51	.788	71	.822	91	
12	.706	32	.752	52	.790	72	.819	92	
13	.710	33	.754	53	.792	73	.814	93	
14	.713	34	.756	54	.794	74	.806	94	
15	.716	35	.758	55	.795	75	.803	95	
16	.718	36	.760	56	.797	76	.810	96	
17	.721	37	.761	57	.799	77	.810	97	
18	.723	38	.763	58	.801	78	.811	98	
19	.726	39	.764	59	.803	79	.810	99	
20	.728	40	.766	60	.805	80	.805	100	

Residuum.

In concluding this communication, I must state that I have obtained valuable information from A. Wurtz's *Dictionnaire de Chimie;* also from a paper published by H. Cornwall, in the *Scientific Monthly;* from *Dana's Geology;* and from THE PROCEEDINGS OF THE AMERICAN CHEMICAL SOCIETY.

XXI.—New Process for the Rapid Estimation of Pure Sugar in Raw and Refined Commercial Sugars.

By P. CASAMAJOR.

Received June 14, 1879.

Part First.

The process for the estimation of sugar, which I propose to describe this evening, is based on a happy idea of M. Dumas. It cannot but be a matter of surprise that, although this idea was published several years ago, it has never been taken up and studied by the numerous chemists whose business it is to analyze sugar.

As an introduction to the subject, I will recall to your memories the main points relating to the process of M. Dumas, and, as this process was suggested to its eminent author, while studying that of Payen, we may also say a few words of the latter.

In 1846, Payen published a process for determining the amount of pure sugar in commercial sugars, which seems to conform more closely to the ordinary processes of chemical analysis than is the case with those which have been more generally adopted for testing sugars. This process consists in washing commercial sugars with alcohol previously saturated with pure sugar. The object of this operation was to wash out everything except the pure sugar, and this, after being freed from the sugar-saturated alcohol by washing with absolute alcohol, could be dried and weighed, as is done with other substances submitted to chemical analysis. Payen found, however, that the quantity of sugar obtained in this way was always less than the actual quantity present. He seems afterwards to have paid very little attention to this process, and apparently did not attach much importance to it.

It was reserved for Dr. Scheibler, of Berlin, in these latter years, to discover that the result obtained by the process of Payen was not the quantity of pure sugar present, but that it represents the *rendement*, or quantity of sugar obtainable in refining. It cannot but be a matter of surprise that Dr. Scheibler did not distinctly claim this discovery, instead of pretending that he had, in a manner, re-discovered the process of Payen, "which had fallen into the domain of history," when, indeed, he had only attached to it cumbersome paraphernalia, which really added nothing to the value of the process.

Payen used two alcoholic solutions saturated with sugar, and finally absolute alcohol, to wash out the last traces of the sugar-saturated solutions. The first solution was obtained by taking alcohol at 85 per cent., and adding to this 5 per cent. of strong acetic acid. This mixture was saturated with sugar. I believe that this addition of 5 per cent. of acetic acid was to decompose the sucrates, which were a great bugbear to the sugar chemists of those days. This addition of acetic acid fulfills, however, a useful purpose, as it seems to make the mixture better able to remove the impurities of gummy sugar.

This first solution of Payen was the one adopted by M. Dumas, and here is the process which he proposed for analyzing commercial sugars :

If we introduce an alcohometer of Gay-Lussac in the first solution of Payen, we find that it sinks to a point which, if we operate at 15° C., corresponds to 74 per cent. If we take a certain volume of this solution and stir it up in a glass with a sufficient quantity of a sugar to be analyzed, we are able to ascertain, by again placing the alcohometer in the solution, that this has taken up something from the commercial sugar, for the alcohometer no longer indicates 74 per cent., but a lower degree, corresponding to a greater density. The process which M. Dumas proposed was this : Take 100 cubic centimeters of the first solution of Payen, and 50 grammes of sugar ; agitate the mixture in a glass ; filter the solution, and observe the alcohometric degree corresponding to 15° C. For every per centage of sugar less than 100, you will find that the solution indicates 1 per cent. less than 74.

A simpler way of stating the same thing is to note that the difference between 100 and 74 is 26, and, if the above proposition is correct, we can obtain the percentage of sugar by adding 26 to the alcohometric degree. Thus, if the alcohometer indicates 68, the percentage of sugar is $68 + 26 = 94$.

The only account I have seen of this process is in L'Abbé Moigno's *Saccharimétrie Physique, Chimique et Mélassimétrique ;* this is translated in the *American Chemist* of February, 1871, p. 302. This description may also be found *verbatim* in a recent work of M. Maumené on sugar.

The account of the process of M. Dumas, as found in the above paper, states that, for sugars having 87 per cent. or more of pure sugar, the results agree very closely with those of the saccharometer,

even within $\frac{1}{10}$ of 1 per cent. For sugars of lower grade, the results obtained were not satisfactory.

After making a great number of tests with the solution used by M. Dumas, I am in a position to state that it is not possible, even with sugars of high grade, to obtain results at all approaching those of the optical saccharometer, when we operate on such sugars as we have in this market. The sugars to which the process was applied in France, may have been beet sugar of about the same grade and similar composition. With our cane sugar, both raw and refined, the differences between the results of the saccharometer and those of the alcohometer were sometimes as high as 3 or even 4 per cent. for sugars above 87 per cent. As to beet sugars, I regret to say that, since I undertook these researches, I have not been able to obtain any samples to form an idea of their behaviour with this process of M. Dumas.

At any rate, as nearly one-half of the raw sugars that come to this market stand below 87 per cent., there seemed to be little use in a process which was declared to be inapplicable to sugars of low grade. I found, however, after trying the process several times, that, although the results obtained were mostly unfavorable, it was impossible to dismiss it entirely, for, upon reflecting upon these results, I found that many questions arose which required to be solved, and, on their solution, I based the hope of modifying this process so as to apply it to the analysis of cane sugars of all grades.

In considering commercial sugars, with the view of applying to them the process of M. Dumas, there are several points which experience has shown to be worthy of attention. Several other points, which have taken a great deal of my time, were found to be of no importance whatever in the study of this question.

To understand the points that are of importance in this inquiry, we may consider that a commercial sugar is composed of four classes of substances :

1st. Pure sugar.

2d. Water.

3d. Soluble impurities, or other soluble substances, besides pure sugar.

4th. Sand, earth and other insoluble substances.

We may now examine each class separately.

1st. The behaviour of pure sugar with the saturated alcoholic solution used by M. Dumas, is easily understood. This solution being incapable of dissolving any further quantity of sugar, its density cannot be affected by the addition of pure sugar alone.

2d. An addition of water lowers the alcoholic degree. When an excess of sugar is present, the alcohol, diluted with water, is able to dissolve an additional quantity of sugar, which still further increases its density. To ascertain the quantities of pure sugar which alcohol of various strengths will hold, I took several saturated solutions and introduced them in the tube of the saccharometer. The results of the observations thus obtained are given in Table No. 1. In the first column of this table is the percentage of alcohol before being saturated with sugar; in the second column is the indication of the alcohometer for the same alcohol, after this has been saturated; in the third column is the direct reading of the optical saccharometer (Ventzke's), when the saturated solution is placed in its tube. Finally, in a fourth column, I have placed the number of grammes of sugar in 100 cubic centimeters of the saturated alcohol. The quantities in this fourth column are calculated from those in the third, by taking 0.26 gr. of sugar as corresponding to one degree of the saccharometer scale.

TABLE No. 1.

DEGREE OF THE ALCOHOMETER BEFORE SATURATION.	DITTO AFTER SATURATION.	DEGREE OF THE SACCHAROMETER.	GRAMMES OF SUGAR IN 100 CC.
92.	91.	2.2	0.572
87.	82.3	.....	.....
85.	79.5	12.2	3.17
84.	78.	14.6	3.80
82.4	74.	19.3	5.02
80.	67.62	26.3	6.83
75.	48.55	50.	13.01
50.	sp. gr. 1.14	192.	49.9

We may notice, in the above table, that if we compare alcohol of 85 per cent. with alcohol of 80 and 75 per cent., that a fall of 5 per cent. from 85 to 80, answers to a difference of 11.88 per cent. in the corresponding saturated solutions, while a fall of 5 per cent. from 80 to 75 corresponds to a difference of 19.07 per cent. in their saturated solutions.

These facts are of prime importance in this inquiry, and we will have occasion in the sequel to draw from them consequences worthy of attention.

3d. *Soluble Impurities.*—To study the effect of soluble impurities on alcohol saturated with sugar, I prepared quite a large quantity of inverted sugar by heating with hydrochloric acid. The acid was afterwards thrown down as chloride of lead, and a small quantity of lead which remained in solution was precipitated with carbonate of soda, but not enough of this reagent was used to make the solution alkaline. This solution was evaporated over a water bath, and the result was, on cooling, a very stiff gummy substance of light yellow color. The presence of a slight excess of sodic chloride did not interfere with the usefulness of the product, as it merely acted as the representative of the soluble impurities of commercial sugar, and these always contain soluble salts.

The effect of dissolving inverted sugar in alcohol saturated with sugar, was to lower the alcohometric degree, and this lowering was progressively greater, as the quantity of inverted sugar was increased. Thus, 5 grammes of inverted sugar lowered the alcohometric degree 11.63 per cent., and 10 grammes lowered it 24.5 per cent., while, if the decrease had been strictly proportional to the quantity of inverted sugar, 10 grammes should have given $11.63 \times 2 = 23.26$ per cent. We may note, however, that the lowering of the alcoholic degree by inverted sugar, which here stands as the representative of the soluble impurities, although not exactly proportional to the quantity added, is more nearly so than is the case with equivalent quantities of water, as we may see in Table No. 1.

4th. *Insoluble Impurities.*—These have no effect whatever on the density of an alcoholic solution saturated with sugar. With clean, dry sand, as well as with pure, dry sugar, no effect takes place in the density of the alcoholic solution. When insoluble substances occur in appreciable quantities, they should be deducted from the indication of the alcohometer.

It must be understood that in the experiments which are related above with water and inverted sugar, an excess of pure, dry sugar was always present. Otherwise the results obtained would not have been applicable to the analysis of sugars.

Although four classes of substances have been mentioned as worthy of consideration, only water and the soluble impurities have any influence in the results obtained by the process of M. Dumas. If a certain weight of water lowered the alcohometric degree to exactly the same extent as an equal weight of soluble impurities, the process proposed by M. Dumas could, by taking a less weight of

sugar for 100 cc of solution, be made to yield accurate results; but this does not happen, and if we have, for instance, a sugar containing 94 per cent. of pure sugar, the other constituents may be either 6 per cent. of water or 6 per cent. of impurities, or any sum of impurities and water amounting altogether to 6 per cent. In each of these cases we may obtain a different result. On the other hand, as the addition of a certain quantity of water gives very different results, according to the strength of the alcohol solution, we can conceive that, by a series of experiments, we may succeed in obtaining a solution of such strength, that, within the limits which correspond to commercial sugars, the results in lowering the alcoholic degree may be practically the same for a certain quantity of water, as for the same quantity of soluble impurities.

Following up this idea, I made a great many experiments, to ascertain whether it was not possible, by raising or lowering the alcohometric degree of a saturated sugar solution, to obtain exactly the strength that would give the required result. In this connection, I may mention, that at an early stage of my experiments, I discarded the use of acetic acid, and I operated with mixtures of alcohol and water only. I found that the solution used by M. Dumas could be replaced by alcohol of 82.4 per cent., saturated with sugar. I tried other solutions, some stronger and others weaker, and I was not long in finding that the bad results obtained with either the solution of M. Dumas or with alcohol of 82.4, saturated with sugar, were much aggravated when the solutions had less alcoholic strength. By a series of experiments, I finally came to the conclusion that a solution of 87 per cent. alcohol would give the most satisfactory results. Alcohol of this strength, when saturated with sugar, stands at 82.3 by the alcohometer. This solution answered very well with sugars of quite high grade, but when I came to apply it to gummy sugars, the impurities would not dissolve, and the results obtained were always a great deal too high. I sought to remedy the evil by taking alcohol at 94 per cent., and lowering the degree with acetic acid instead of water, because, as I have said, acetic acid has a favorable action in dissolving gummy impurities, but I did not succeed in effecting this object, and, much to my disappointment, I had to give up, for a time at least, the project of applying the idea of M. Dumas to the analysis of cane sugars.

Part Second.

I had given up the hope of success, when, on passing before No. 71 Maiden Lane, I saw at a window a number of bottles, labelled

Diamond Methal, which proved to be methylic alcohol. I determined to try if methylic alcohol would answer better than the ethylic, and purchased a gallon of the product. This stood at 92.5 degrees by the alcohometer, and even at this strength, the gummiest sugar could be cleansed by mixing with this spirit and stirring the mixture. On saturating it with sugar, and placing the solution in the tube of a Ventzke saccharometer, the indication was 1.7, which is less than corresponds to ethylic alcohol of the same density.

These first trials were very encouraging, and those that followed were not less so. Without recounting now the experiments that were made, I may state that, by the use of methylic alcohol, I finally succeeded in obtaining, with an alcohometer, results that agree very closely with those of the optical saccharometer, with cane sugars of all classes, from the highest to the lowest.

The explanations already given concerning the use of ethylic alcohol of various strengths, saturated with sugar, and the effects that water and the soluble impurities have in lowering their alcohometric degrees, render superfluous any account of similar experiments with hydrate of mythyl. I may briefly state that, after making a great number of trials, I found that methylic alcohol of 83½ degrees of the alcohometer,* when saturated with sugar, stands at 77.1 degrees, and that this solution is the one that has given the most accurate results.

This saturated solution is quite easily obtained by taking methylic alcohol standing at 83½ degrees by the alcohometer, and saturating it with sugar, by the process which Numa Grar suggested to Payen. This consists in shaking up the alcohol with powdered sugar. Grar made his powdered sugar by grinding it in a mortar in presence of alcohol. I have generally used dry *extra-powdered* sugar. When this cannot be had, grinding in a mortar is an excellent way of getting the sugar in fine particles, which are very necessary for obtaining a saturated solution in a short time. When very finely powdered sugar is shaken up with either ethylic or methylic alcohol, the finest particles are dissolved almost immediately, while the coarser

*Since this paper was written, I have found the following interesting coincidence: The alcohometric degree 83½, corresponds to a specific gravity of 0.85315 (Prof. MacCulloch's tables for Tralles' alcohometer). On consulting Dr. Ure's table for methylic alcohol (Phil. Mag. [3], XIX, 51), it may be seen that specific gravity 0.8531, corresponds to 87 per cent. of methylic alcohol. Now, in the first part of this paper, I have said that ethylic alcohol of 87 per cent., saturated with sugar, gives the results which agree most closely with those of the optical saccharometer.

grains fall to the bottom, leaving the liquid quite clear after standing a minute or two. When the alcohol clears up in this way, it is an indication that it is not saturated, and an additional quantity of sugar should be shaken up with it. This is repeated until the mixture remains cloudy for at least two or three minutes after adding finely powdered sugar. When this takes place, the liquid is saturated, and a further addition of sugar will not increase its density. By operating in this way, we may obtain saturated alcohol in 10 or 15 minutes, while, by hanging sugar crystals in the solution, I have not been able to obtain the maximum of density in less than two days. When we are about to use the solution, it is advisable to shake it up a little while before using it, and, after the sugar has been deposited, to take the alcohometric degree. This degree cannot be higher than that shown by previous observations, but it may become lower, if the bottle is not tightly closed, as the alcohol evaporates, leaving a residuum containing a greater proportion of water. There is no use in placing chloride of calcium tubes on the cork of the bottle in the vain hope that, in this way, water may be absorbed from the atmosphere. The lowering of the alcoholic degree takes place principally by the evaporation of the spirit, and nothing can replace tight stoppers. The tin cans, with screw caps, that are used for refined petroleum, are well adapted for holding methylic alcohol, and of these, Coleman's *elevated swinging cans* are the most convenient for holding our standard solution.

When on testing the saturated alcoholic solution, we find that the degree is lower than required, we may raise it by adding more alcohol. The addition of alcohol causes the precipitation of a part of the sugar in solution, so that the quantity of alcohol to be added should be somewhat less * than the quantity to be added to a mixture of alcohol and water, of which we desire to raise the degree by the addition of stronger alcohol.

If we have a certain volume, V, of alcohol and water, whose alcohometric degree is d, and we wish to raise this degree to D, with strong alcohol of degree $\triangle$, if the volume of the latter alcohol to be added is called x, we shall have

$$Vd + x\,\triangle = (V+x)\,D,$$

whence

$$x = \frac{V\,(D-d)}{\triangle - D}$$

If we have 1000 cc of alcohol at 81, and we wish to raise the degree to 83½, with alcohol of 92 per cent., then d=81, D=83½, V=

* I usually take 0.8 x.

1000 and $\triangle = 92$, and the volume of alcohol of 92 to be added, is

$$x = \frac{1000 \times 2.5}{8.5} = 294.1 \text{ cc.}$$

If the addition of alcohol has been too great, we may diminish the degree by adding water very cautiously, and stirring up the mixture with an excess of sugar. To obtain the quantity of water, we may use the above formula, but we must note that $\triangle = 0$, and, as both numerator and denominator have become negative quantities, we may change the signs, and we shall have :

$$x = \frac{V\ (d - D)}{D}$$

These particulars have been entered into, because of the great importance of obtaining saturated solutions which do not deviate too widely from 77.1 degrees of the alcohometer. Too much attention cannot be given to this, as otherwise it is not possible to obtain correct results.

Next in importance, is the weight of commercial sugar to be taken for 100 cubic centimeters of the methylic solution saturated with sugar. In the process proposed by M. Dumas, 50 grammes of sugar are stirred with 100 cubic centimeters of his standard solution. At the outset of the experiments on this process, I found that one obvious cause of error was the imperfect solubility of the impurities of commercial sugars in this standard solution. I was led then to grind the sugar down in a mortar as thoroughly as possible, so as to break up all the lumps and crush the large crystals, to allow everything to dissolve that would. I used for this quite a heavy pestle, of a size quite disproportionate to that of the mortar. By this thorough crushing, much less sugar is used than M. Dumas proposed. It is an easy matter to determine the quantity of sugar to be used in a test. At first we may take an arbitrary quantity, and note the result, which may be corrected by the following considerations. The lowering of the alcohometric degree depends, as we have said, on the water and the soluble impurities present in the sugar. If we take a certain weight of sugar, say 45 grammes, we may find by the alcohol process that the result is 91.5 per cent. of sugar. If we test the same sugar by the optical saccharometer and find 93 per cent. of sugar, we know that the alcohol process has given us too low a result, and this because the solution was too dense. Our result shows in the sugar : 100—91.5=8.5 of impurities and water, while we ought to have had 100—93=7. We must then, to obtain 93, take a weight equal to $\frac{45 \times 7}{8.5} = 37.05$ grammes.

After trying many experiments with solutions of different strengths, it was found that each solution required a different weight. For the saturated solution of 77.1 degree of the alcohometer, which is our standard solution, the weight is 39.6 grammes for 100 cubic centimeters of the solution.

Instead of using 100 cubic centimeters, I have, for a long time, used only 50. To be able to use a cylinder in which this volume would give indications, I needed to use alcohometers of quite small diameter. These were made by Mr. H. Weinhagen; they are very well graduated and very satisfactory in every way.

For 50 cubic centimeters of standard solution, the proper weight is half of the one for 100 cubic centimeters = 19.8 grammes. To show how this was obtained, the following table, No. 2, is given. In the first column are numbers designating the sugars that were tested; in the second column is the per centage of sugar as obtained by the optical saccharometer; in the third column is the result by the methylic alcohol process, when we take 19 grammes as the weight of the sugar tested; in the fourth column is the quantity that should have been taken, instead of 19 grammes, to obtain the same result as by the optical saccharometer. These weights were obtained by the calculation already given.

TABLE No. 2.

SUGAR.	DEGREE OF SACCHAROMETER.	RESULT BY METHYLIC ALCOHOL. Weight, 19 gr.	WEIGHT TO GIVE RESULTS IN 2D COLUMN.
			gr.
1	91.6	91.9	19.7
2	84.8	85.36	19.66
3	91.7	92.1	19.96
4	81.7	82.46	19.8
5	88.8	89.1	19.7
6	96.3	96.6	20.6

From the results in the 4th column, the weight adopted was 19.8 gr.

By using this weight, with 50 cubic centimeters of standard solution, the following results were obtained in the case of 15 consecutive tests of raw and refined sugars:

TABLE No. 3.

DESIGNATION OF THE SUGAR.	PER CENTAGE OF PURE SUGAR BY SACCHAROMETER.	DITTO BY METHYLIC ALCOHOL.	DIFFERENCE.
Muscavado.....	82.4	82.3	—.1
"	91.5	91.7	.2
Refined.....	95.	95.1	.1
Molasses.....	86.5	87.2	.7
Centrifugal.....	96.5	96.2	—.3
Refined.....	96.3	96.6	.3
"	92.3	92.1	—.2
"	91.3	90.9	—.4
"	84.4	83.7	—.7
"	91.6	91.5	—.1
"	84.8	84.7	—.1
Raw.....	91.7	91.8	.1
Refined.....	81.7	81.7	.0
Muscavado.....	88.7	88.7	.0
Centrifugal.....	96.3	96.5	.2

The greatest deviation shown in this table, is in the case of two sugars, in which the difference is 0.7. This is not due to impurities affecting the saccharometer, as I found by inverting the solution of the sugar in each case. In one of the sugars I found quite a number of soft lumps, which showed that the sugar was very uneven. In the other sugar nothing was found to account for the discrepancy.

The alcohometers used in these tests are those of Tralles, which are used by the United States Government. These do not differ materially from those of Gay-Lussac. They are more apt to differ from one another on account of defective construction, than they should do from Gay-Lussac's instrument.

Alcohometers, like other areometers, are very unreliable, unless placed in the hands of those who understand their use. We may, however, use alcohometers that are not strictly accurate, if only the divisions of the scale bear to one another the proper proportion, and if the displacement of the scale is not too great. This does not apply to the preparation of the standard solution, which should stand correctly at 77.1, which degree of the alcohometer of Tralles corresponds to specific gravity 0.87.

When we use an alcohometer that is properly graduated, and we have the standard solution standing at 77.1, we should add 22.9 to the

degree of the alcohometer at 15° C., to obtain the per centage of sugar. If the alcohometer, through being defective, should not stand at 77.1 for 0.87 specific gravity, but at 76.5, the difference between this latter number and 100, being 23.5, this is the number to be added to the reading of the areometer at 15° C., to obtain the percentage of sugar in the sample under examination.

I have said that cane sugars of all grades, from the highest to the lowest, have given satisfactory results by this process. This assertion is borne out by the examples in Table No. 3. I wish, however, to call attention to this, that I do not comprise, under the head of sugars, melados or molasses. As to melados, those that have drained out and are comparatively dry, may be classed as sugars, but wet melados give very poor results. This may be very easily understood, if we remember what was said of the action of water in lowering the alcohometric degree of a saturated solution, as exemplified in Table No. 1. I have little doubt, however, that by experimenting with saturated solutions of methylic hydrate of higher alcoholic degree, we may obtain a solution specially adapted for testing wet melados. It might even be possible, with methylic hydrate of still higher alcohometric degree, to test molasses within certain limits of density. As an operator can always tell beforehand, whether what he has to test is properly a sugar, a wet melado or a sample of molasses, he could always use the saturated solution which was the best adapted to his sample.*

From past experience, with saturated solutions of various strengths, I may venture the opinion that methylic alcohol of 87 degrees of the alcohometer, saturated with sugar, would make a good standard solution for wet melados. For molasses of density, about 40° Baumé, methylic alcohol of 90½ degrees (alcohometer), saturated with sugar, would not, as far as I can judge without trying it, be far from the proper strength. These are merely hints thrown out to chemists who are interested in testing sugar. Should I not work out these sugges-

*With melados and molasses, as well as with very low sugars, the direct test seldom gives the true per centage of sugar. It is necessary to invert, to obtain the correct result, and when we invert a solution that has been imperfectly decolorized, it becomes so red, after inversion, that it is a difficult matter to see through the tube. With chloride of tin and filtration over bone black, it is possible to improve the color of the solutions, but even these often fail. The bone black should be dry and not too great a quantity should be used. On account of these difficulties with dark solutions, experiments to establish the strength of the standard solution and the weight of sugar, may have to be made entirely with refined syrups or with low grade refined sugars, to which 5 or 6 per cent. additional of water should be added.

tions, I hope that others may find time to study them. The advantages of a process that allows a commercial saccharine product to be tested in about five minutes, are too great to be neglected. The weights of melado or molasses to be taken, would have to be determined, as was done for the weight 19.8 grammes, as shown in Table No. 2.

Correction for variations of temperature.—When we operate at temperatures different from 15° C. or 60° F., the corrections can be made by using either the tables of Gay-Lussac or those for the instrument of Tralles, which we owe to Prof. MacCulloch. I will, however, state that results that are sufficiently accurate, may be obtained by proceeding as follows :

For solutions which give, by the alcohometer, from 77 to 70, we may multiply the excess of temperature above 60° F. by 0.2, and deduct the product from the reading of the alcohometer. For degrees of the alcohometer between 70 and 60, we may multiply this excess by 0.205, and for indications below 60 degrees of the alcohometer, the excess of temperature above 60° F., must be multiplied by 0.21, and the product deducted. If a centigrade thermometer is used, the excess of temperature over 15° should be multiplied by 0.36 for solutions above 70 degrees of the alcohometer. For solutions between 60 and 70 degrees (alcohometer), the excess over 15° C. should be multiplied by 0.37, and for those below 60, this excess should be multiplied by 0.38. In all cases, the product should be deducted from the direct reading of the alcohometer. The results obtained in this way do not differ materially from those given by the tables.

There is another correction for variation of temperature, which relates to the volume of standard solution to be taken for a weight of sugar equal to 19.8 gr. As the temperature rises, a greater volume of standard solution should be taken. If we use a Farenheit thermometer we take

At 60° F.....	50.	cc of	standard	solution
" 70° F.....	50.3	"	"	"
" 80° F.....	50.6	"	"	"
" 90° F.....	51.	"	"	"
"100° F.....	51.3	"	"	"

If we use a centigrade thermometer, we should take

At 15° C.....	50.	cc of	standard	solution
" 20° C.....	50.25	"	"	"
" 25° C.....	50.5	"	"	"
" 30° C.....	50.8	"	"	"
" 35° C.....	51.2	"	"	"
" 40° C.....	51.4	"	"	"

If it should be preferred to use always the same volume of 50 cc of standard solution, we may take the following weights for the temperatures of a centigrade thermometer

At 15° C.....19.8 grammes.
" 20° C.....19.7 "
" 25° C.....19.6 "
" 30° C.....19.5 "
" 35° C.....19.4 "
" 40° C.....19.3 "

In the following table may be found the same data concerning methylic alcohol of various strengths, saturated with sugar, as are given in table No. 1 for ethylic alcohol.

TABLE NO. 4.

DEGREES OF THE ALCOHOMETER BEFORE SATURATION.	DITTO AFTER SATURATION WITH SUGAR.	DEGREE OF THE SACCHAROMETER (VENTZKE).	GRAMMES OF SUGAR IN 100 CC.
92.5	91.8	1.7	0.44
83.5	77.1	13.2	3.43
82.7	76.5	....	....
81.5	75.	....	....

From this table we may learn that the solution, saturated with sugar, standing at 77.1 by the alcohometer, should, when placed in the saccharometer tube, stand at 13.2. We also learn that the same saturated solution must contain 3.43 grammes of sugar in 100 cc. This is a useful guide for the quantity of extra powdered sugar that should be added to 1 liter of methylic alcohol of 83½°.*

*From this table we may also learn that if we apply methylic alcohol to Payen's process, we need have no fear of leaving in the sugar a small quantity of the solution made by saturating with sugar methylic alcohol at 92.5 degrees. With ethylic alcohol, cane sugars are always left with too much impurity. Dr. Behr informs me, that on this account, he has never been able to obtain good results by this process. It is certainly worth while trying methylic alcohol. Cane sugars could be washed out with our standard solution, testing 77.1 (alcohometer), and the last particle of this could be removed by methylic alcohol 92.5, saturated with sugar. The small quantity of this latter remaining after filtration, would leave too little sugar to cause an appreciable error. The funnel with auxiliary vertical tube, of which I gave a description several years ago, is very well adapted to washing sugars out with alcohol, as it leaves them quite dry without the help of a filter pump (see *American Chemist*, Oct., 1875, Vol. vi, p. 122, and *Chemical News*, Vol. xxxii, No. 829, p. 183).

Method of Procedure in Testing.—The sugar to be tested should not be weighed before every thing is ready, as otherwise it may dry out, after being weighed, and give too high a result. The mortar and pestle should be clean and dry, the cylinder should be filled with the standard solution to a line indicating 50 cubic centimeters, and a clean dry funnel should be ready with a paper filter in it. The weight of sugar to be taken is 19.8 grammes. This is transferred to the mortar as soon as weighed, and the standard solution should be poured in the mortar, and the sugars then ground with a heavy pestle until all lumps and large crystals are broken up.*

The mortar I have used for grinding sugar in presence of the standard solution, has a capacity of 180 cubic centimeters, and the pestle is of such a size, that it displaces 80 cubic centimeters in this mortar.

After all the lumps have been broken up, the contents of the mortar are poured on a filter standing over the cylinder, which previously held the standard solution. As there was some of this solution left in the cylinder, about 10 cubic centimeters of the filtered solution is allowed to run into the cylinder, after which the funnel is taken from the cylinder and held over the mortar long enough to shake up the liquid in the cylinder and pour it back on the filter. After this the funnel is placed again over the cylinder, the contents of the mortar are poured again on the filter, and from 30 to 35 cubic centimeters are allowed to run through the filter, which are generally sufficient for a test. In this filtered solution are placed, in succession, an alcohometer and a thermometer. To the alcohometric degree, corrected for temperature, is added the difference between 100 and the alcohometric degree of the standard solution. This sum represents the per centage of sugar.

Example.—The standard solution gives with the alcohometer 76.8, when corrected for temperature. The same alcohometer, placed in the filtered solution, marks 71 degrees, while a centigrade thermometer shows a temperature of 28°. According to what has been already

*Persons who test raw centrifugal sugars by this process, must very soon see what *artificially colored sugars* consist in. This has been a vexatious question, occupying the attention of eminent chemists. By washing sugar crystals with alcohol, we may easily see that in the grains of some of them have been incorporated brown insoluble particles. In some cases these look like the scum from the defecation of the juice, and, in other samples, the coloring matter seems to be clay or some brown pigment This coloring matter seems generally to have been added in a very clumsy manner, as after washing the crystals in alcohol, it may be seen in lumps, specking the crystals with dark dots.

said, we take the difference between 28 and 15=13, and multiply this difference by 0.36, the product being 4.68. This quantity subtracted from 71, gives 66.32. The difference between 100 and 76.8 being 23.2, this quantity is added to 66.32, and the sum, 89.52, is the quantity of pure sugar in the sugar tested.

It has been suggested that the evaporation of methylic alcohol during the manipulations that have been described, must interfere with the accuracy of the results obtained, but this does not seem to be the case. It might be possible to avoid evaporation entirely by leaving out the operation of grinding the mixture of sugar and methylic alcohol in a mortar, but, in this case, the results obtained would be less accurate on account of the impurities left in the sugar. Beyond avoiding working in a draft, no precaution has been taken to prevent evaporation. One reason why the evaporation of the alcohol seems to have so little effect on the result, is that the operations of grinding and filtering occupy only a few minutes, during which no appreciable loss takes place.

XXII.—Contributions from the Laboratory of the Stevens Institute of Technology.

By ALBERT R. LEEDS.

I.—SOLUBILITY OF OZONE IN WATER.

Schoenbein, in his numerous papers, taught that ozone is insoluble in water, and this statement was thence transferred to the accounts given of the properties of ozone by other writers, and finally adopted as a universally admitted fact in chemical text-books.*

Williamson (1845),† arrived at conflicting results with regard to the solubility of ozone and, it should be added, with reference to ozone itself. He ascribed the peculiar properties belonging to the the oxygen set free by electrolysis, to the admixture of a *peroxide or acid of hydrogen*. This body, according to Williamson, even when formed by the electrolysis of oxide of copper dissolved in sulphuric acid (in order that no hydrogen might be liberated at the same time), and after careful drying by calcium chloride, yielded when passed

*"On Schoenbein's Ozone:" Faraday, Proc. Royal Inst., vol. i, p. 94. Elements of Chemistry: Miller, 1860, vol. ii, p. 23.

†"Some Experiments upon Ozone:" Phil. Mag., xxvii, p. 372. Chem. Soc. Mem., ii, p. 395. Liebig's Ann., liv, p. 127.

over heated copper, a notable amount of water. In his final experiments, the copper was reduced by carbonic oxide rather than hydrogen, which was at first employed, for fear that in the latter case, the copper might retain occluded hydrogen.* This kind of ozone communicated to water through which it was passed, the characteristic odor and the property of decomposing potassium iodide. But the ozoniferous air, prepared by driving moist air through a tube filled with pieces of phosphorus, did neither. In another experiment, when the air after passing over the phosphorus entered directly into a solution of iodide and starch, decomposition took place. Finally, a long and wide tube was filled with pieces of phosphorus, which were placed alternately. By heating the tube thus filled, the phosphorus was partly melted into the asbestos and partly sublimed upon it; thus exposing a far greater surface than in the former experiments. After complete cooling, atmospheric air was driven through the tube into the iodide and starch, but not the slightest reaction was produced. These different reactions are explained by Williamson, on the supposition that in the case where the iodide was decomposed, the phosphorus did not expose sufficient surface to absorb all the oxygen, and a mixture of phosphoric acid and oxygen went over, which by their simultaneous action on the potassium iodide set iodine free. But as soon as sufficient surface was given to the phosphorus all oxygen was absorbed, phosphoric acid alone was carried over, and the mixture of iodide and starch was not affected.

Concerning these results it is to be remarked:—

1st. Air ozonised by phosphorus, contains so small a percentage of ozone, that it must be passed through water at ordinary temperatures for a long time, to communicate to it the property of decomposing potassium iodide. If the wash-water is surrounded by ice, it acquires this virtue in a much shorter period (several hours). The decomposition is due in part to the hydrogen peroxide, which is likewise present. It is not owing to phosphorus or phosphoric acid, since these bodies do not directly decompose potassium iodide, nor to oxides of nitrogen, since the only one present is nitric acid.

2d. Since electrolytic ozone was soluble in water, while that produced by the action of phosphorus on atmospheric air was not, Williamson thought he was dealing with two different substances.

* Repeated experiments, made since this time, have abundantly justified the necessity of this precaution. And inasmuch as water was apparently formed by reduction, the ozoniferous gas produced by electrolysis was regarded as a peroxide of hydrogen. This again was held to be different from Thenard's peroxide, since the latter is not odorous, nor, as stated by Williamson, volatile.

Schoenbein immediately assailed Williamson's results,* and reiterated his oft-repeated declaration that the matter of the ozone produced in both cases was identical, an assertion abundantly verified by many subsequent experimenters.

3d. Schoenbein also pointed out that in the final experiment with phosphorus, which Williamson regarded as conclusive, the finely divided phosphorus would destroy, by combining with it, the ozone as rapidly as formed.

SORET, in a paper entitled "Experiments on Ozone,"† states that he obtained by electrolysis, oxygen containing in 105 parts, 2 parts of ozone. But when the gas was collected under water, and absorbed with potassium iodide after all the gas had been disengaged, less oxygen was found, because water dissolves a considerable proportion (about one-fifth of the ozone liberated in an experiment in which the water was analyzed).

MEISSNER, by prolonged contact of ozoniferous air, which had been ozonised by phosphorus and then agitated with water, with a little water obtained a liquid which exhibited the chemical reactions of ozone.‡ HOUZEAU likewise found that water which had been in contact with ozone, manifested the ozone reactions. §

MARIGNAC, in the 12th section of the memoir,‖ in which he overthrew the second hypothesis of Schoenbein, that nitrogen was a compound body of which ozone was one of the elementary constituents, stated that ozone undergoes no absorption nor alteration by *water*, concentrated sulphuric acid, calcium chloride, ammonia or baryta-water.

ANDREWS states ¶ that ozone, from whatever source prepared, "is not absorbed by water, but when sufficiently diluted with other gases, is destroyed by agitation with a large quantity of water; it is also contrary to the common statements, destroyed by being agitated with lime-water and baryta-water, provided a sufficient quantity of these solutions be used."

CARIUS, last of all, re-investigated the question with great pains and multiplied experiments.** His method was as follows: the ozonised oxygen employed was prepared by the electrolysis of cold

* Phil. Mag., xxvii, p. 451.
† Phil. Mag., xxv (1863), p. 209.
‡ Untersuch. ueber d. Sauerst., Hanover, 1863.
§ Berichte der deutsch. chem. Gesell., vi, p. 603.
‖ Compt. Rend. (1845), p. 808.
¶ Proc. Royal Soc., vii (1856), p. 476.
** Berichte der deutsch. chem. Gesell., vi, p. 520.

diluted sulphuric acid, with platinum iridium electrodes, after the plan of Soret.* It was passed for about two hours into water, kept at a temperature of +0.5° to 3°. The proofs of the fact of absorption having occurred, were, according to Carius:

I.—The strong and characteristic odor.

II.—The blueing of iodide-potassium-starch solution, and its subsequent bleaching by further addition of the ozone-water.

III.—Oxidation of thallous to thallic oxide.

IV.—Bleaching of indigo and litmus, and blueing of guaiacum tincture.

V.—The gas evolved from the solution and collected, showed the above reactions, and also acted upon manganese and lead papers, with formation of peroxide.

VI.—When fresh, bleached litmus paper, after several days, did not alter them (absence of nitrous acid).

VII.—It did not develope a blue color with acid potassium chromate and ether. After warming to 30° and 40° from ½ to 1 hour, it no longer turned iodide-potassium-starch blue, even after addition of ferrous sulphate (absence of hydrogen peroxide).

Carius likewise determined by means of potassium iodide solution, the coefficient of solubility of ozone at various temperatures. For temperatures between 0.5° and 3.2°, the amount of ozone absorbed in a liter of water was (mean of 3 trials) 9.4 mgrms, or 4.4 cc at 0° and 760 mm.

Unfortunately, Carius found that the commercial "ozone-water" of Krebs, Kroll & Co. (Berlin), in which he had disproved the presence of nitrous and nitric acids and hydrogen peroxide, gave the same reactions as the solution of ozone, which he had prepared himself. Moreover, it contained according to Carius, 9.55 mgrm or 4.45 cc ozone per liter. Shortly after, C. Rammelsberg† examined this commercial ozone-water, and found that every sample examined, afforded a precipitate with silver nitrate. In one instance, the precipitate corresponded to 16 mgrms chlorine per liter. Carius replied‡ to this, that the "commercial ozone-water" which he had employed, manifested only the very faintest opalescence with silver nitrate, and had not affected silver foil immersed in it. In his earlier communication, he had stated with reference to the effect of ozone-water on silver, that the latter was not blackened in case it were entirely im-

*Compt. Rend., lvi, 390.

†Berichte der deutsch. chem. Gesell., vi, p. 603.

‡ib., vi, p. 809.

mersed in the water, but if not, and a little space was left in the flask above the water, a very perceptible blackening occurred. In one such successful trial, the commercial "ozone-water" was used, in another, that prepared by himself. In two other similar trials, with the latter, *no blackening occurred.*

In other words, the proof of the solubility of ozone adduced by Carius, breaks down at the most important point; that is, whether or no such water has the power of forming silver peroxide upon silver which has been immersed in it. For not only is the silver test free from the objections, which might possibly be urged against the validity of the other tests, but if successful, would show that the ozone *after absorption*, retains a characteristic which is perhaps the one most illustrative of its energetic oxidizing power—that of being able to convert silver into the state of peroxide. It was determined, therefore, in attacking the problem again, to use more severe tests than those hitherto employed, and that among these the oxidation of silver, while completely immersed in water, should play a conspicuous part. Moreover, it was desirable to have a slow stream of the ozonised gas passing over, rather than through the water. As a convenient method of realizing these conditions, three of the phosphorus ozonators were placed in connection with one another.

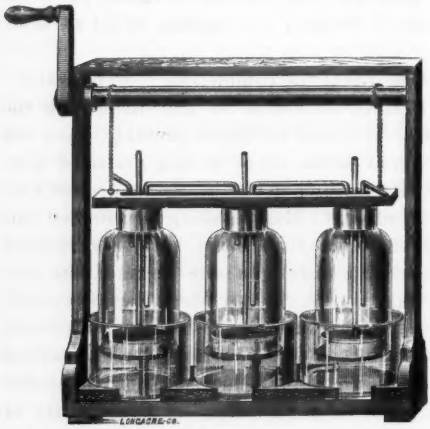


FIG. 1, PHOSPHORUS OZONATOR. (First Form.)

Since these ozonators have been considerably modified, subsequent to the description originally published (JOUR. AM. CHEM. SOC., Vol. I, p. 10), we have introduced besides Fig. 1, representing the old form, a new wood-cut, Fig. 2, showing various improvements. These are briefly:

1. A washing tube, 25 cm long and 3 cm diameter, plugged with damp cotton-wool, and fastened along the cross-bar of the apparatus, so as to intervene between the exit tube and kerite tubing, and filter out oxides of phosphorus, etc. In most cases it is greatly to

be preferred to a wash bottle. A similar washing tube, plugged with amianthus moistened with alkali, is in like manner attached to the inlet tube when it is desired to purify from carbonic acid the air employed.

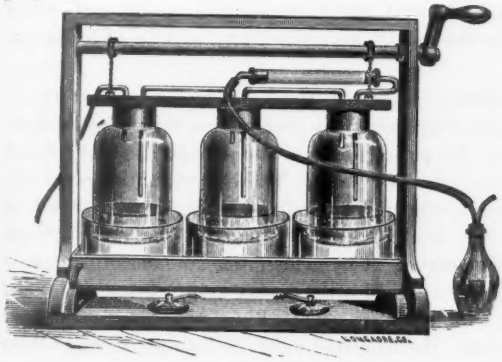


FIG. 2, PHOSPHORUS OZONATOR.
(Latest Form.)

2. The movable rods and stages are done away with, and the phosphorus cakes are supported on leaden discs, which rest on leaden brackets let into holes bored through the bells a little way above their lower rims.

3. The jars rest upon cross-pieces at the bottom of a long copper water bath, beneath which lamps are placed so as to retain the temperature at the point of maximum evolution of ozone (24°). These tanks are also provided with inlet and exit pipes so as to permit of the jars being cooled by a current of water, if desirable.

First experiment.—This experiment was instituted to determine (*a*) whether a difference existed in the rate of oxidation of lead plates, when immersed in aerated and in ozonised water, (*b*) whether lead sulphide was ozonised to sulphate, and (*c*) whether silver was peroxidized under like circumstances. The inlet tube of the first ozonator was connected with a soda-lime V-tube, to remove the carbonic acid. The weight of the lead disc ordinarily used to support the phosphorus cakes, was determined before beginning of experiment. The jar in which it was immersed contained distilled water. The exit tube of the first ozonator was connected with the inlet tube of the second, which was arranged with phosphorus in the ordinary manner, and used to generate the ozone. In order to remove the oxides of phosphorus, ammonium nitrate and hydrogen peroxide from the ozonised air, it was connected by means of kerite tubing with a long glass tube stuffed with damp cotton-wool, which effects this washing more thoroughly than an ordinary wash bottle. This cotton purifier was again connected by kerite tubing with a third ozonator. In this,

the first bell contained a sheet of silver plate partly immersed in the distilled water of the jar; the second bell, a leaden disc painted over with white lead and previously blackened by exposure to hydrogen sulphide; the third bell, simply a weighed leaden disc. Both these discs were supported as usual, and were parallel to the surfaces of the distilled water in the second and third jars, at a depth of about 1 cm.

Air was continuously aspirated through the apparatus for 7½ days, about 1800 liters containing 2.5 grms ozone being drawn over.

(*a.*) At the end of this period, dense white precipitates had formed in both jars containing the lead plates. These precipitates were crystalline in character, presenting octahedral planes, and consisted of hydrated protoxide of lead. The lead plate in the bell through which air was drawn weighed 265.5 grms; the amount of hydrated oxide of lead produced, weighed after drying 0.4671 grm. The lead plate in the bell through which ozonised air was drawn, weighed originally 375.75 grms; the hydrated oxide of lead produced, 0.8802 grm or nearly twice that in the case of the water which had been in contact with air only.

(*b.*) The sulphide of lead was completely bleached.

(*c.*) The silver plate was blackened above the surface of the liquid, where it was in direct contact with the ozonised air, but not below.

Second experiment.—It was highly probable, therefore, that the ozone had gone into solution, since otherwise the increased production of hydrated lead oxide and the bleaching of lead sulphide, could hardly be accounted for. But inasmuch as negative results had been obtained in what might fairly be regarded as the crucial test—blackening of the silver plate—the experiment was repeated, though in a somewhat different manner. One of the phosphorus ozonators was attached to the kerite delivery tube of an electrical ozoniser. In one of the bells, a flat dish containing freshly precipitated and carefully washed lead sulphide was suspended, so that the lead sulphide should be immersed 1 cm below the surface of the water. In the second bell, a sheet of silver foil was placed, the lower half immersed in a slanting direction. A slow current of ozonised air, containing 24 mgrms of ozone per liter, was passed through the ozonator for 3½ hours. The lead sulphide was not noticeably affected; the silver plate above the liquid was black and deeply corroded. Below the surface a number of flakes of oxide were found, which on removal left stains upon the silver that could not be washed or rubbed off.

Third experiment.—This was undertaken because we had not succeeded above in bringing about the oxidation of lead sulphide and silver at one and the same time. 5 filter papers of 12 cm diameter were saturated with lead acetate, blackened with hydrogen sulphide and dried. They were then fastened to one another and to the bottom of a flat crystallizing dish, with a few drops of paraffine, and sufficient water poured into the dish to cover the paper to the depth of about 1 cm. The dish was then supported on the leaden brackets of the bell, so that it might be gently lowered into the water of the jar, without disturbing anything. A silver plate 15 cm in diameter was similarly arranged in the second bell. It had been polished with gypsum and alcohol, rinsed with caustic potash, then with alcohol, and finally completely immersed to the depth of 1 cm without handling. 30 liters of ozonised oxygen, containing in all 0.72 grm ozone, were passed in a frequently intermitted current into the apparatus, during an interval of 48 hours. Shortly after the operation began, a film appeared on the surface of the dish containing the lead papers, and increased until at the close it had become a pellicle with high lustre and of dark brown color. Under the microscope, no traces of crystalline structure were apparent, but the scales exhibited a beautiful dark red translucency. They dissolved in hydrochloric acid with evolution of chlorine, and proved to be anhydrous peroxide of lead.*

The liquid was strongly acid to litmus paper, and gave a precipitate with barium chloride, showing the presence of a notable amount of free sulphuric acid. In other words, the lead sulphide, under these circumstances, had become oxidized, not to lead sulphide as was anticipated, but into free sulphuric acid and anhydrous peroxide of lead.

The silver was not perceptibly affected until towards the end of 24 hours, when faint stains began to appear and increased until, at the end of 48 hours, they corresponded to about $\frac{1}{20}$th the area of the plate. These films floated up to the surface, and had a dark grey color. On washing and drying the plate, its surface formerly like a mirror, was found to be similarly corroded.

Conclusion.—These results, it appears to us, are conclusive as to the much disputed point, whether or no ozone is soluble in water. Moreover, the oxidations effected appear to show that it retains even in solution, its maximum of oxidizing power. The *fact* of the solu-

* Dr. G. E. Moore, who repeated the microscopic examination with the use of much higher magnifying powers than I had employed, was likewise unsuccessful in finding any indications of crystalline structure. Moreover, according to Dr. Moore's observations, the scales do not appear to be doubly refracting.

bility having been established, there would seem to be no objection to adopting the approximate coefficients of solubility at various temperatures, as determined by Carius.

II.—ACTION OF OZONE UPON THE COLORING MATTER OF PLANTS.

In the Annals of N. Y. Academy of Sciences, Vol. i, No. 7, p. 216, I have given the results obtained when ozonised oxygen was made to act upon flowers and plants. They were exposed to the action of a slow continuous current of ozonised oxygen containing 1 mgrm ozone per liter, during intervals varying from 18 to 36 hours. The results, which were mainly negative, were so unsatisfactory, that I have repeated them with the aid of more efficacious apparatus for generating ozone.

One phosphorus ozonator was employed to supply ozone, another, without the phosphorus cakes upon the discs, made a convenient arrangement to contain the flowers. As their stems were placed in vessels filled with water, and the bells were closed by the water contained in the jars, the atmosphere surrounding the flowers was kept moist, which was of importance in the conduct of the experiment.

1. BLEACHING OF FLOWERS (152 liters of air pased over).

	After 10 hours (120 mgrms ozone).	After 19 hours (228 mgrms).
Heliotrope,	Dirty yellow. (Leaves bleached at ends.)	Bleached, leaves also. All perfume destroyed.
Bouvardia,	Yellow at end of petals.	Partly bleached. Leaves white in spots.
Violet,	White in spots.	Some petals white.
Pink,	Little affected.	Little affected.
Pansy (purple),	White in spots.	More bleached.

At the end, therefore, of 19 hours, when 152 liters of air containing in all 228 mgrms of ozone had passed over, the bleaching was very imperfect.

2. 1200 LITERS OF AIR PASSED OVER (total ozone 1.8 grms).

	At the end of 5 days.
Lantana, red,	Yel'w and somewhat decomposed.
Fuchsia, calyx, carnation—red,	Yellow.
petals, rose-pink,	Dirty white.
Petunia, magenta-colored,	Calyx and petals partly bleached.
Rose, crimson,	Yellow.
Agapanthus umbellatus,	White at end of petals.
Verbena, purple with wh. centre,	Bleached.
Pelargonium, scarlet,	"
Euphorbia, salmon-colored,	Partly bleached.
Fuchsia,	Calyx and stamens yellow.
Verbena, maroon-colored,	Dirty white.

A piece of calico with a pattern in black and bright green was completely bleached during the same interval, the green color having disappeared completely, and the stain of the mordant only remaining where the black had been.

3. Ozonised Oxygen (exposed for 3½ hours).

Rose, light red,	Nearly white, leaves white in spots.
Fuchsia,	Bleached to light red.
Verbena, purple,	White with purple spots.
" red,	White with red spots.
Petunia, purplish-red,	White in spots.
Pelargonium, pink,	White at end of petals.
Bouvardia,	Dirty white.

No determination was made of the percentage of ozone during this particular experiment. But the same ozoniser was employed as in other trials, when it had produced 24 mgrm ozone per liter. A slow current of the gas was kept flowing during the course of the entire experiment.

Conclusion.—The coloring matters of both leaves and flowers of the species experimented upon, were destroyed by ozone. But a considerable percentage of ozone is required to produce this result, or if such small amounts as are obtained in the customary methods of ozonising air by phosphorus are employed (1 to 3 mgrms per liter), a large volume of ozonised air must be used, and a considerable interval elapse, before bleaching is effected.

III.—BLEACHING OF SUGAR SYRUPS BY OZONE.

Not being able to find in chemical journals, any accounts of experiments made upon colored syrups with ozone as a bleaching agent, while there were rumors that such experiments had been tried, although with very partial success, it appeared the easiest way of obtaining satisfactory knowledge upon this point, to make suitable trials in this laboratory. The material was kindly furnished by Dr. Arno Behr, from syrups manufactured in the refinery of Messrs. Matthiessen & Wiechers, Jersey City. The first specimen, was of syrup which had undergone but one filtration, and was of a brownish-yellow color. In this preliminary experiment, the amount of ozone required to effect the bleaching was not determined. At its close, the syrup was of a faint straw-color and of slightly acid reaction.

A second trial was made upon a syrup which had been twice filtered, still retaining a strong yellow tint. 20 cc of the syrup were

introduced into a Geissler absorption apparatus, and a slow current of oxygen, ozonised to the extent of 24 mgrm ozone per liter, was passed through it for several hours. When about 100 mgrm ozone had been brought into contact with the syrup, it had become almost colorless. To our litmus paper it was neutral, although Dr. Behr informs me he detected a very faint acid reaction.

As determined by Dr. Behr, the filtered syrup when it came from the refinery, contained in 100 parts, 50 parts of dry substances and 40 parts of pure sugar. The alteration in bleaching, is seen in the following table.

EFFECT OF OZONE UPON FILTERED SYRUP.

Dry substance contains.	Unbleached.	Bleached.
Cane sugar (by polariscope) - -	79.7 per cent.	80.0 per cent.
Inverted sugar - - - -	12.7 "	12.7 "

IV.—REDUCTION OF CARBONIC ACID BY PHOSPHORUS AT ORDINARY TEMPERATURES.

As a preliminary determination, rendered essential in the progress of certain studies, it became necessary to ascertain whether phosphorus was entirely without action upon carbonic acid at ordinary temperatures. The inquiry was set on foot with the expectation merely of arriving at a negative result. The experiment was conducted as follows: the three leaden discs of the phosphorus ozonator were covered with cakes of fresh phosphorus, and lowered beneath the surface of the water in the jars. After the air had been completely expelled by a very long continued current of carbonic acid, the cakes were raised so as to bring them in contact with the gas. As it issued, the gas flowed through a potassium iodide wash bottle, and then through a Peligot tube, containing strips of paper saturated with solution of palladium chloride. After 5 hours, the iodide was unaffected, but the palladium papers were blackened, and the liquid at the bottom of the V-tube contained a notable precipitate. On replacing the papers by fresh ones, they were blackened in the course of 15 minutes. Allowed to remain over night (16 hours), and aspirated with proper precautions through solution of palladium chloride, the latter showed an increase in weight of 40 mgrms.

Two wide-mouthed flasks were filled with carbonic acid, great precautions being taken to exclude air. Each contained several sticks of phosphorus, partly covered with water. After sealing, one was placed in the dark, the other in sunlight, and both allowed to remain

for 24 hours. As in the preceding experiments, dense fumes arose in both bottles, those in the bottle exposed to sunlight being attended with the deposit of much sublimed yellowish-red phosphorus. On testing the contents, both flasks gave straightway the carbonic oxide reaction.

Finally, a quantitative determination of the amount of carbonic oxide produced, was made in the following manner: a 5 liter jar was entirely filled with water, the air in the generating apparatus and the various wash bottles, etc., was removed by a long continued current of carbonic acid, and at last the jar was filled with the gas, the last traces of oxygen having been taken out by the interposition of a wash bottle containing potassium pyrogallate. After standing for 4 days in contact with the phosphorus and water at bottom of the jar, the residual gas was drawn off; first, through a long moist cotton filter, then through a potassium iodide solution, then through 3 V-tubes, filled respectively with $CaCl_2$, Cu_2Cl_2 and $CaCl_2$, the last acting as a guard. The iodide solution underwent no change, but the acid solution of cuprous chloride had absorbed 0.150 grm of carbonic oxide.

Formation of phosphuretted hydrogen in the course of this reduction.—Of scarcely less interest and novelty, was the generation of hydrogen phosphide during the reduction of carbonic acid. This fact was at once made strikingly apparent on opening the flask above mentioned, and which had been exposed to the sun, by the very powerful and characteristic smell. On plunging a strip of paper wet with silver nitrate into the gas, a dense precipitate of silver was formed immediately. This reduction of the silver salt did not occur on immersing similar strips in an atmosphere of carbonic oxide. The reaction which occurs in these cases is not improbably correctly represented in the equation:

$$6\ P+5\ CO_2+3\ H_2O=P_2O_5+P_2O_3+2\ PH_3+5\ CO.$$

Mutual reactions of water and phosphorus.—The foregoing results raised the question whether the hydrogen of water might not deport itself, at common or somewhat elevated temperatures, towards phosphorus as a basic radical and, in this case, the water undergo decomposition according to the equation:

$$P_4+6\ H_2O=2\ H_3PO_3+2\ PH_3.$$

To answer this question, water which had been boiled for a number of hours in order to expel the air, was digested for 48 hours, at a temperature of 92°–96° with phosphorus, and the minute amount of gas, given off, collected and examined. Not a trace of hydrogen phosphide was found, thus negativing the above hypothesis.

V.—OXIDATION OF CARBONIC OXIDE BY AIR OVER PHOSPHORUS AT ORDINARY TEMPERATURES.

Having demonstrated, by some preliminary experiments, that carbonic oxide was converted into acid by air over moist phosphorus at common temperatures, the following experiment was made, in order to determine the amount of carbonic acid formed. A 5 liter jar containing 5 sticks of phosphorus and a little water, was filled with 2500 cc of carbonic oxide and the remaining space with air. The carbonic oxide was made from potassium ferrocyanide and sulphuric acid, and washed with water, caustic potash and baryta water. On transferring it to the jar, it was washed again in similar manner, a final V-tube filled with baryta water remaining pellucid, showing the absence of any carbonic acid. The air was purified likewise. At the expiration of 18 hours, the gases were drawn first through a moist cotton filter, then through a potassium iodide solution, and finally through two baryta waters. The faint rose coloration which the iodide solution struck with starch water, corresponded to 0.04 mgrms ozone in the total volume of gas drawn over ; the last baryta water remained clear, the first had absorbed 14 mgrms carbonic acid. The carbonic acid estimation was made by decomposing the barium salt, and weighing the carbonic acid gas evolved, for fear that some traces of oxides of phosphorus might have escaped the purifiers, and entered into combination with the baryta.

Experiments instituted in order to determine whether *pure* carbonic oxide, subjected to the action of moist phosphorus, for long periods and in some cases with the conjoint action of sunlight, would result in the reduction of the carbon compound to some lower oxide or to the elementary condition, gave a negative result.

Abstracts from American and Foreign Journals.

Justus Liebig's Annalen der Chemie.

Abstractor, GEO. A. PROCHAZKA, PH. D.

Nitrosalicylic Acids, and the Isomerisms of the benzol-derivatives, H. HUEBNER (Ann. Chem., **195**, 1–55).—In the same manner in which, starting from metabrombenzoic acid, the author had formerly deduced two orthohydrogen atoms in the monosubstituted benzol, he proves the existence of two metahydrogen atoms, by a similar series of substitutions, with salicylic acid as a starting point:

Orthohydroxybenzoic acid or salicylic acid, $C_6H_4\begin{cases}^{o}OH\\ ^{1}\\ CO_2H\end{cases}$, by nitration, yields two metanitroorthohydroxybenzoic acids:

$$C_6H_3\begin{cases}^{o}OH\\ \alpha m\\ NO_2\\ ^{1}\\ CO_2H\end{cases} \qquad C_6H_3\begin{cases}^{o}OH\\ \beta m\\ NO_2\\ ^{1}\\ CO_2H\end{cases}$$

α metanitroorthohydroxybenzoic acid; β metanitroorthohydroxybenzoic acid.

The diethyl ethers of these acids on treatment with alcoholic ammonia, yield:

$$C_6H_3\begin{cases}^{o}NH_2\\ \alpha m\\ NO_2\\ ^{1}\\ CO_2H\end{cases} \qquad C_6H_3\begin{cases}^{o}NH_2\\ \beta m\\ NO_2\\ ^{1}\\ CO_2H\end{cases}$$

α orthoamidometanitrobenzoic acid; β orthoamidometanitrobenzoic acid, which by azotation yield:

$$C_6H_4\begin{cases}^{m}NO_2\\ ^{1}\\ CO_2H\end{cases}$$

metanitrobenzoic acid.

It will be seen that the two isomeric nitrosalicylic acids furnish, in substitution of their hydroxylgroups by hydrogen, the same metanitrobenzoic acid, showing that they contain two hydrogen atoms in metaposition with reference to the carboxyl group.

The different position, in the two acids, of the hydroxyl group, with reference to the nitro group, can be easily demonstrated, as the

two mononitrosalicylic acids, on heating with lime, yield two different mononitrophenols:

$$C_6H_3\overset{o}{.}OH\overset{\alpha m}{.}NO_2\overset{1}{.}CO_2H \text{ yields } C_6H_4\overset{1}{.}OH\overset{p}{.}NO_2$$

Paranitrophenol.

$$C_6H_3\overset{o}{.}OH\overset{\beta m}{.}NO_2\overset{1}{.}CO_2H \quad " \quad C_6H_4\overset{1}{.}OH\overset{o}{.}NO_2$$

Orthonitrophenol.

The derivations and derivatives thus outlined are described in detail in the paper. Two series of salicylates are mentioned. $(C_6H_3.X.OH.CO_2)_2\overset{''}{M}$ = semimetalsalicylates; and $C_6H_3.X.\left\{\begin{matrix}O\\CO_2\end{matrix}\right\}\overset{''}{M}$ or $\left\{\begin{matrix}C_6H_3.X.O.CO_2\\ \overset{''}{M}\quad\overset{''}{M}\\ C_6H_3.X.O.CO_2\end{matrix}\right\}$ or $\left\{\begin{matrix}C_6H_3.X.O.CO_2\\ \overset{''}{M}\quad\overset{''}{M}\\ CO_2.O.X.C_6H_3\end{matrix}\right\}$ = metalsalicylates.

Salicylic acid, on treatment with nitric acid, yields the two isomeric mononitrosalicylic acids, one dinitrosalicylic acid, di- and trinitrophenol.

Methods for the preparation of the mononitrosalicylic acids. (1) 50 gms of nitric acid (1.5 sp. gr.) are added in small portions to a cold solution of 100 gms salicylic acid in 500 or 800 gms glacial acetic acid. The resulting liquid is diluted with 2 or 3 vol. water and cooled down very low. (2) 10 gms salicylic acid are gradually added to a mixture of 10 gms fuming nitric and 10 or 12 gms glacial acetic acid; the resulting liquid is poured in 250 cc very cold water. The precipitates obtained in both cases are mixtures, consisting substantially of the two mononitrosalicylic acids. (3) α mononitrosalicylic acid is obtained almost pure by saturating a saturated solution of salicylic acid in cold glacial acetic acid with the fumes generated in the ignition of dried plumbic nitrate. By subsequent dilution with water, a precipitate of almost pure α mononitrosalicylic acid is obtained.

The separation of the two nitrosalicylic acids is effected by appropriate utilization of the difference in solubility in water of the acids and their semibarium salts.

α *metanitroorthohydroxybenzoic*—or α *nitrosalicylic acid*, $C_6H_3\overset{\alpha m}{.}NO_2\overset{o}{.}OH\overset{1}{.}CO_2H$ (m. pt. 228°); long known; long colorless needles, crystallizing without water of crystallization from the aqueous solution. β *nitrosalicylic acid*, $C_6H_3\overset{\beta m}{.}NO_2\overset{o}{.}OH\overset{1}{.}CO_2H + H_2O$ (m. pt. 125°), seems to dissolve in water more readily than the former;

long colorless needles. The dehydrated acid (m. pt. 144°) is hygroscopic.

α monopotassium, m onoammonium, magnesium, barium, semibarium, semistrontium, semicalcium, semizinc, semisilvernitrosalicylate, and β monopotassium, monosodium, barium, magnesium, lead, semibarium, semistrontium, semisilver, semimercury (?) and mercurynitrosalicylate, are described.

α semibariumnitrosalicylate $(C_6H_3.\overset{\alpha m}{NO_2}.\overset{o}{OH}.\overset{1}{CO_2})_2\ Ba+6\ H_2O$, small yellow needles, very soluble in water. β semibariumnitrosalicylate $(C_6H_3.\overset{\beta m}{NO_2}.\overset{o}{OH}.\overset{1}{CO_2})_2\ Ba$, gold colored scales or needles, very little soluble in water.

α monoethylnitrosalicylate, m. pt. 93°, very long, colorless needles, readily soluble in alcohol; β monoethylnitrosalicylate, large colorless plates, very little soluble in cold alcohol; α sodiumethylnitrosalicylate, $C_6H_3.NO_2.ONa.CO_2C_2H_5$, thin yellow needles, readily soluble in alcohol; β salt, yellowish-red needle, little soluble in alcohol; α diethylnitrosalicylate, m. pt. 98°, colorless needles; β diethylether, oily liquid, of agreeable odor.

α nitrosalicylamide, m. pt. 225°; β nitrosalicylamide (145–146°); both long, colorless needles; α potassium, barium, calciumnitrosalicylamide are readily soluble in water; α leadnitrosalicylamide, soluble in a great deal of water; β barium, calcium, and basic β lead nitrosalicylamide are very little soluble in water.

The two nitrosalicylic acids were still further characterized by the preparation and examination of the following compounds: α amidosalicylic acid, α chlorohydroamidosalicylic acid, α sulphuric-amidosalicylic acid, α acetamidosalicylic acid and α magnesium, barium, calcium, zinc-acetamidosalicylate, β amidosalicylic acid; only the hydrochloric acid salt of this acid could be obtained in the same manner (evaporation of the two acids) as the corresponding α amidosalicylic acid compound.

α *metanitroorthoamidobenzoic* or α *nitramidobenzoic acid*, $C_6H_3.\overset{\alpha m}{NO_2}.\overset{o}{NH_2}.CO_2H$, m. pt. 263°; long, very thin lemon-colored crystals with silver lustre; salts described; barium, calcium, potassium, ammonium, (copper,) lead, and the hydrochloric acid salt.—β *nitramidobenzoic acid*, m. pt. 204°, long yellow needles; the salts of this acid with the just mentioned metals and acid, strontium and silver, are described.—β ethylnitramidobenzoate, m. pt. 104°, yellow scales.

Paranitrophenol, long colorless needles, soluble in water, not volatile with water vapor, m. pt. 114°.—*Orthonitrophenol*, m. pt. 45°, difficultly soluble in cold water, very volatile with water vapor.

The diazocompounds, obtained from the two nitramidobenzoic acids, on boiling with alcohol, yield the same *metanitrobenzoic acid* (m. pt. 141–142°), which in each case was identified by the analyses of the acid, the barium and copper salts, and of the metamidobenzoic acid (m. pt. 174°).

Nitration of the nitrosalicylic acids.—This part of the paper embraces the results of the author and H. Behaghel von Adlerskron. The two mononitrosalicylic acids, on further nitration, yield only one and the same dinitrosalicylic acid (dimetanitrosalicylic acid). $C_6H_3.\overset{\alpha m}{NO_2}.\overset{o}{OH}.\overset{1}{CO_2H}$ and $C_6H_3.\overset{\beta m}{NO_2}.\overset{o}{OH}.\overset{1}{CO_2H}$, both yield $C_6H_2.\overset{\alpha m}{NO_2}.\overset{\beta m}{NO_2}.\overset{o}{OH}.\overset{1}{CO_2H}$. These facts demonstrate the frequently occuring regularity, that negative constituents will enter, when acting upon substituted benzole derivates, into ortho and para-relation with reference to the most positive constituent, forming two isomeric compounds, which by further introduction of the same negative constituent, yield the same more highly substituted compound; in this case dimetanitrosalicylic acid.

The comparison of the dinitrosalicylic acids from both sources, of their mono- and dipotassium, monoammonium, monobarium, monocalcium, monolead salts and their monoethyl ethers, establishes that there is no difference between them.

β dinitrophenol $C_6H_3.\overset{o}{NO_2}.\overset{p}{NO_2}.OH$, m. pt. 63–64°, is obtained as a secondary product by the further action of nitric acid on dinitrosalicylic acid. The author reserves the more thorough investigation of this latter reaction for a future period.

Researches upon the Non-saturated Acids, RUDOLPH FITTIG. Second paper (Ann. Chem., **195**, 56–179).

1. Further Contributions to the knowledge of Fumaric Acid and Maleic Acid, CAMILLE PETRI (Ann.Chem., pp. 56–78).–Fumaric acid, when heated with bromine and water, is converted into dibromsuccinic acid. The reaction takes place in the cold, but only very slowly, and on long digestion. Isodibromsuccinic acid is not formed in the reaction.—Maleic acid, by digestion with bromine and water, yields isodibromsuccinic acid and fumaric acid, which latter acid by

the further action of bromine, is converted into dibromsuccinic acid. The reaction takes place readily and rapidly at ordinary temperature.

Dibromsuccinic acid, when boiled with water, is readily and completely decomposed into brommaleic and hydrobromic acids (in contradiction to the statement of Kekulé). The brommaleic acid thus obtained, m. pt. 128°, is identical with Kekulé's brommaleic and so-called metabrommaleic acid.—Isodibromsuccinic acid, in the same manner, yields isobrommaleic acid, m. pt. 177–178°, identical with Kekulé's isobrommaleic acid and so-called parabrommaleic acid.

Brommaleic and isobrommaleic acid, on treatment with nascent hydrogen, both yield fumaric and succinic acid, but not a trace of maleic acid. Maleic acid alone is not converted into fumaric acid by nascent hydrogen.

Both acids, on distillation, yield brommaleic anhydride and water, which combine again, on standing, to brommaleic acid.

Brommaleic acid, on treatment with fuming hydrobromic acid at ordinary temperature, readily yields dibromsuccinic acid; a portion of the acid, however, is converted into the isomeric isobrommaleic acid.—Isobrommaleic acid combines with hydrobromic acid only very slowly at ordinary temperature, rapidly at 100°, yielding the two dibromsuccinic acids.

On treatment with bromine and water, at ordinary temperature, brommaleic and isobrommaleic acid are both converted into tribrom-succinic acid, $\begin{matrix} CBr_2—CO_2H \\ | \\ CBrH—CO_2H \end{matrix}$, m. pt. 136–137°; small, transparent, deliquescent crystals, extremely soluble in water, alcohol and ether, easily in benzol.

Tribromsuccinic acid is decomposed when heated in aqueous solution; carbonic acid escapes, hydrobromic acid and dibromacrylic acid are found in solution. ($C_2HBr_3\begin{matrix} CO_2H \\ CO_2H \end{matrix}=C_2HBr_2-CO_2H+CO_2+HBr$, the probable reaction.)

Dibromacrylic acid, m. pt. 85°, b. pt. 243–250° (under partial decomposition), beautiful, very large lamellar crystals. Barium salt, $(C_3HBr_2O_2)_2Ba + 2\frac{1}{2}H_2O$, quadrangular plates; calcium salt, $(C_3HBr_2O_2)_2Ca + 3\frac{1}{2}H_2O$, beautiful, long, colorless needles; ethyl ether, b. pt. 212–214°, colorless liquid of agreeable odor. Fuming hybromic and dibromacrylic acid yield, at 100–130°, another acid, m. pt. 53°, probably tribrompropionic acid, which it is very difficult to separate from unaltered dibromacrylic acid.

Bourgoin's tribromsuccinic acid differs in all its properties from the acid obtained by the author. A repetition of the experiments of Bourgoin led him to conclude that Bourgoin's acid was a mixture principally of dibromfumaric and dibromsuccinic acids.

The author concludes that brommaleic acid alone is a true derivative of maleic acid, while isobrommaleic acid is in reality bromfumaric acid, thus further confirming the constitutions assigned by Fittig (Ann. Chem., **188**, 95) to fumaric acid and maleic acid

2. Researches upon Oil of Roman Camomile. (Ann. Chem., **195**, 79–130, Roman Camomile=anthemis-nobilis.)

1. *Organic Acids Obtained in the Saponification of Oil of Roman Camomile*, H. KOPP (Ann. Chem., **195**, 81–92).—Saponification effected by alcoholic potash. Fractional distillation of the purified mixture of organic acids yielded: at 150–160°, isobutyric acid and a small quantity of an acid which was not obtained pure, seemingly methacrylic acid; at 181–187°, crystals of angelicic acid; at 187–190°, a liquid mixture of about equal parts of angelicic and tiglic acids; at 190–195°, crystals of tiglic acid. Valerianic acid, the ethers of which, according to Demarçay, form the main constituents of the oil, or other acids, could not be found. The quantities of angelicic acid and tiglic acid obtained were nearly equal, the quantity of isobutyric acid being much smaller.

Angelicic acid, $C_5H_8O_2$, m. pt. 45–45.5°, b. pt. 185°. Tiglic acid, $C_5H_8O_2$, m. pt. 64.5°, b. pt. 198.5°, identical with Geuther's tiglic acid, obtained from croton oil, and Frankland's and Duppa's methylcrotonic acid. The tiglates are much less soluble in water than the angelicates. Calcium angelicate, $(C_5H_7O_2)_2\,Ca + 2\,H_2O$, much more soluble in cold than in warm water; calcium tiglate, with $3\,H_2O$, dissolves much more easily in hot than in cold water; barium angelicate $(C_5H_7O_2)_2\,Ba + 4\frac{1}{2}H_2O$, very soluble in water; tiglate $(C_5H_7O_2)_2Ba + 4H_2O$; potassium angelicate, very soluble, deliquescent; tiglate, $C_5H_7O_2K$; silver angelicate and silver tiglate, $C_5H_7O_2\,Ag$, white feathery crystals.

The author confirms the statement of Demarçay that, by the action of heat or concentrated sulphuric acid, angelicic acid is converted into tiglic acid. Pure angelicic acid had been almost completely converted into tiglic acid, after 40 hours boiling.

2. *The Separate Constituents of Oil of Roman Camomile*, JULIUS KOEBIG (Ann. Chem., **195**, 92–108).—By very repeated fractional distillation, the oil was divided into five principal portions. By the analysis of each of these, and by saponification with aqueous potash

in each case, it was shown that the oil consisted of a mixture of various compound ethers. It does not contain an aldehyde, or any appreciable quantity of a terpene (result in accordance with Demarçay). The following ethers were found as constituents:

Isobutyric-isobutyl ether, angelicic-isobutyl ether, angelicic and tiglic-amyl ether; the angelicic and tiglic ethers of a new hexyl alcohol; and the angelicic and tiglic ethers of a terpene alcohol, designated as anthemol.

The oil began to boil at 140°; the thermometer rose regularly, and with comparative rapidity to 180°. Most of the oil distilled between 180 and 200°; the thermometer did not remain stationary, however, at any single point for any length of time. The distillation was interrupted at 220°, when partial decomposition begins. About one-third of the oil remained behind in the distillation flask.

Fraction boiling at 147–148°, much smaller in bulk than any of the other portions; principally an isobutyric ether, presumably isobutyric-isobutyl ether, containing also a small quantity of what appears to be a hydrocarbon. Fraction of 177–177.5°, $C_9H_{16}O_2$, thin colorless liquid of agreeable camomile odor, consists of angelicic-isobutyl ether, $C_5H_7O–O–C_4H_9$. Fraction of 200–201°, $C_{10}H_{18}O_2$, colorless, pretty viscous liquid of camomile odor, principally angelicic-amyl ether, containing also a small quantity of the isomeric-tiglic ether. Fraction 204–205°, $C_{10}H_{18}O_2$, similar to the former, a mixture of angelicic and tiglic amyl ethers, the latter preponderating. Residue at 220°, dark brown liquid, contains the angelicic and tiglic ethers of the hexyl alcohol, and the angelicic and tiglic ethers of anthemol.

The yield of the various alcohols from the separate fractions was small. Fractional distillation of the mixture of alcohols, obtained in the saponification of the oil with alcoholic potash, yielded them in larger quantity, admitting the verification of their properties. Isobutyl alcohol, $C_4H_{10}O$, b. pt. 107–108°; further verified by the preparation of the calcium isobutyrate. Amyl alcohol, b. pt. 129–130° (fermentation amyl alcohol?). Hexyl alcohol, $C_6H_{14}O$, b. pt. 152–153°, thin liquid of strong, not disagreeable odor; sp. gr.=0.8295 (15°). It is a primary alcohol, different from the normal. (The lime salt of the acid it yields on oxidation, corresponds in its formula to capronate, but is neither capronate nor isocapronate.) Anthemol, $C_{10}H_{16}O$, viscous colorless liquid of peculiar camphor odor, b. pt. 213–214.5°, distils under partial decomposition (polymerisation?). The acetic ether, $C_{10}H_{15}O–C_2H_3O$, b. pt. between 232–238°, is a viscous oily liquid. A mixture of bichromate of potash and sulphuric acid,

acts very energetically upon anthemol. Concentrated nitric acid converts it into a brown resinous mass. On boiling with dilute nitric acid, anthemol yields paratoluic, terephtalic and perhaps terebinic (?) acid.

The author arrives at the conclusion that the tiglic ethers are real constituents of the oil.

3. *Contributions to the Knowledge of Angelicic Acid and Tiglic Acid*, ALEXANDER PAGENSTECHER (Ann. Chem., pp. 108–128). —The separation of the acids was effected by appropriate application of the difference in the behavior of their lime salts to the solvent action of water.

Tiglic acid and angelicic acid, on treatment with highly saturated hydrobromic acid at ordinary temperature, both yield bromhydrotiglic acid From tiglic acid very nearly the theoretical amount is obtained, much less from angelicic acid. This latter acid besides bromhydrotiglic acid yields also other products, more soluble in carbon disulphide, the nature of which it was not possible to determine (bromhydroangelicic acid?).

Bromhydrotiglic acid, $C_5H_9BrO_2$, as obtained from the carbondisulphide solution, large clear colorless plates (crystallographic description by Bücking and Schimper); insoluble in cold water, decomposed by hot water; easily soluble in carbondisulphide; m. pt. 66–66.5°. The acid dissolves readily in aqueous sodium carbonate solution; the solution evolves carbonic acid and pseudobutylene (identified by the analysis of the bromide $C_4H_8Br_2$, b. pt. 156–158°). Most of the acid is decomposed according to the equation $C_4H_8Br—CO—ONa=C_4H_8+CO_2+NaBr$; a small quantity of the acid, however, is reconverted into tiglic acid. By prolonged boiling with water the acid is almost completely reconverted into tiglic and hydrobromic acids; a small portion of the acid is decomposed into pseudobutylene, carbonic acid and hydrobromic acid.—On proper treatment of bromhydrotiglic acid with nascent hydrogen, hydrotiglic acid in considerable quantity and very little of another solid acid, were obtained. This latter acid (m. pt. 184–194°) dissolves with difficulty in cold water, pretty easily in hot water, is not volatile with water vapor and corresponds to the formula $C_{10}H_{18}O_4$, appearing to be a bibasic acid, isomeric with sebacylic acid.

Hydrotiglic acid, $2\ C_5H_{10}O_2$, b. pt. 177°, sp. gr.=0.941 (21°); thin colorless liquid, little soluble in water; odor similar to that of valerianic acid, but much weaker. The acid appears to be identical with

the ethylmethylacetic acid ($CH_3—CH_2—CH\begin{matrix}CH_3\\COOH\end{matrix}$), described by Saur, and the acid obtained by Schmidt and Berendes from tiglic acid by the action of hydroiodic acid. Calcium salt $(C_5H_9O_2)_2\,Ca+5\,H_2O$, long, colorless, efflorescent crystals, more soluble in warm than in cold water; silver salt, $C_5H_9O_2Ag$, voluminous white precipitate or colorless feathery crystals. Ethyl ether, $C_4H_9—CO_2C_2H_5$, colorless mobile liquid, of very pleasant fruit odor.

On treatment with bromine, tiglic and angelicic acids both furnish dibromhydrotiglic acid. The former yields nearly the exact theoretical amount and no oily byproduct (Schmidt and Berendes); angelicic acid yields about 70 p. c. of the theoretical amount and byproducts, the exact nature of which could not be determined.

Dibromhydrotiglic acid, large, colorless, well developed crystals (crystallographic description given in the original), insoluble in cold water, decomposed by hot water; easily soluble in carbondisulphide; m. pt. 86–86.5°. By heating the acid with water in sealed tubes to 100°, these were obtained as decomposition products: carbonic acid, monobrombutylene, tiglic acid and a small quantity of a syruppy, non-volatile substance, which was very soluble in water. The same products were obtained on boiling the acid with water. The acid is easily decomposed at ordinary temperature by sodium carbonate solution. Ample quantities of monobrombutylene (C_4H_7Br, b. pt. 86–88°, colorless, oily liquid of piercing odor) are formed. The products obtained by the action of nascent hydrogen on dibromtiglic acid vary, as it seems, according to the conditions under which the experiments have been performed. Tiglic acid was among the products obtained.

The authors conclude that the derivatives described are derivatives of tiglic acid, not of angelicic acid.

4. *Constitution of Tiglic Acid and Angelicic Acid*, R. FITTIG (Ann. Chem., **195**, 128–130).—The author considers the question of the constitution of tiglic and angelicic acids an open one. The results obtained confirm for tiglic acid the constitutional formula generally assigned to methylcrotonic acid, $CH_3—CH=C\begin{matrix}CH_3\\COOH.\end{matrix}$

Thus: $CH_3—CH_2—CH\begin{matrix}CH_3\\CO—OH\end{matrix}$ Hydrotiglic acid.

$CH_3—CH_2—CBr\begin{matrix}CH_3\\COOH\end{matrix}$ Bromhydrotiglic acid.

$CH_3—CHBr—CBr\begin{matrix}CH_3\\COOH\end{matrix}$ Dibromhydrotiglic acid.

3. Upon Non-saturated Aromatic Acids (pp. 131–179).

1. *Addition Products of Cinnamic Acid*, RUD. FITTIG and F. BINDER (Ann. Chem., **195**, 131–143).—Erlenmeyer and Swarts independently allowed hydrobromic or hydrochloric acid to act upon cinnamic acid at high temperature; the products obtained were principally carbonic acid and an oil, pronounced by the former as distyrol, $C_{16}H_{16}$, by the latter, as halogen styrol. In consequence of the high temperature applied they failed to obtain addition products.

Bromhydrocinnamic acid, $C_9H_9BrO_2$, is obtained in almost theoretical yield at ordinary temperature by the action of hydrobromic acid, saturated at 0°, on cinnamic acid. The acid is purified by recrystallization from boiling carbon disulphide. Colorless crystals, with mother-of-pearl lustre, m. pt. 137°; very easily soluble in alcohol and ether, soluble with difficulty in cold carbon disulphide. Between 137–150° the acid is completely decomposed into cinnamic acid and hydrobromic acid; byproducts had not formed in appreciable quantity.

Iodohydrocinnamic acid, obtained in like manner by the action of hydroiodic acid on cinnamic acid, dissolves more readily in carbon disulphide than the former. Colorless crystals, becoming slightly colored on standing; m. pt. 119–120° under partial decomposition (separation of HI and iodine).

The two acids are identical with the compounds obtained by Glaser by the action of hydrobromic and hydroiodic acid on phenyllactic acid. The acids are completely decomposed at ordinary temperatures, or even at 0°, by sodium carbonate solution. The following reactions take place:

$$C_9H_8BrO_2Na = C_8H_8 + NaBr + CO_2$$
$$C_9H_8BrO_2Na = C_9H_7O_2Na + HBr$$
$$C_9H_8BrO_2Na + H_2O = C_9H_8(OH)O_2Na + HBr.$$

Styrol is the principal product; the reaction in fact furnishes the best method for its preparation. Phenyllactic acid (Glaser's) and cinnamic acid are formed only in small quantities. Styrol, C_8H_8, b. pt. 144–144.5°, colorless oil, which on standing completely transforms into colorless glassy metastyrol. Both acids, brom and iodohydrocinnamic acids, are decomposed on boiling with water. The former yields phenyllactic and hydrobromic acid as principal products, cinnamic acid and styrol as byproducts; the latter, cinnamic acid and hydroiodic acid principally, phenyllactic acid and styrol as byproducts.

Dibromhydrocinnamic acid (prepared by Schmitt as early as 1863) is very easily obtained by very gradual addition of the calculated quantity of bromine, in carbon disulphide solution, to the carbon disulphide solution of cinnamic acid. According to the different statements of Schmitt, Erlenmeyer and Glaser, the acid furnishes, on boiling with water, β bromstyrol, carbonic acid, bromphenyllactic acid, cinnamic acid and resinous products. The authors confirm these results in general. Glaser observed the formation of cinnamic acid and resinous products, which *they* attribute to impurities of his material. Glaser's bromstyrol, which according to him distilled at 228° without decomposition, was not pure. Besides β bromstyrol, another compound, which cannot be distilled without decomposition (α bromstyrol), is evidently also formed in the reaction. Bromstyrol was obtained as a white crystalline mass (m. pt. + 7°), solidifying again completely at 0°. It distilled completely between 219–221°; the formation of hydrobromic acid was very perceptible in the distillation; the distillate did not solidify again as completely as before at 0°. Bromstyrol and bromine yield bromstyroldibromide, $C_8H_7Br_3$, m. pt. 37–38°, long colorless needles. Dibromhydrocinnamic acid is a little more stable to sodium carbonate than the monobrom acid. Upon standing, a difficultly soluble, crystalline sodium salt forms, which seems to be stable at ordinary temperature, which, however, is decomposed, if the temperature be even slightly raised.

2. *Notice on Amidohydrocinnamic Acid* (*phenylamidopropionic acid*), ED. POSEN (Ann. Chem., **195**, 143–145).—Bromhydrocinnamic acid yields on treatment with concentrated aqueous ammonia at 0°, styrol, amidohydrocinnamic acid, cinnamic acid and possibly phenyllactic acid. Amidohydrocinnamic acid, $C_6H_5—CH_2—CH\langle^{NH_2}_{COOH}$ somewhat difficultly soluble in cold water, easily in hot water, easily in alcohol, almost altogether insoluble in ether and carbon disulphide. Large, colorless, well developed crystals, m. pt. 120–121°. Basic or acid properties not very pronounced.

The authors are engaged in further utilizing this reaction in the preparation of similar amido acids, more especially in the synthesis of tyrosine.

3. *Atropaic and Isatropaic Acid*, RUD. FITTIG and C. WURSTER (Ann. Chem., **195**, 145–168).—*Tropaic acid*, transparent needles or plates; easily soluble in water, almost insoluble in carbon disulphide; m. pt. 117–118°; not volatile with water vapor. The acid is not altered by the action of water, even at 130° in sealed tubes. On boil-

ing with concentrated baryta hydrate solution, it yields atropaic acid and other products.

Atropaic acid was prepared by prolonged boiling of atropine with baryta hydrate solution; 100 pts atropine yield from 44–46 pts of the acid. The acid obtained by recrystallization from boiling water is impure, containing isatropaic acid. The pure acid, obtained by recrystallization from dilute alcohol (1 alcohol, 1 water), presents beautifully glistening, colorless lamellar crystals; m. pt. 106–107°. Under reduced pressure it can be distilled without decomposition. It is volatile with water vapor (in contradiction to Kraut's statement).

Isatropaic acid.—If atropaic acid is gradually heated from 100–140°, and maintained at the latter temperature for some time, it becomes solid, in consequence of its conversion into isatropaic acid. This transformation can be also effected by boiling the acid with water. Isatropaic acid is very difficultly soluble in hot water, and appears to be insoluble in cold water. It is almost insoluble in ether, carbon disulphide (characteristic difference from atropaic acid), benzol and ligroin; more readily soluble in alcohol. The warm saturated aqueous solution, on cooling and standing, deposits the acid only very slowly, in the form of a crystalline powder. Glacial acetic acid yields it in small colorless, well developed crystals; m. pt. 240–240.5°. Slight impurities lower the melting point considerably (Lossen's acid, m. pt. 200°).

If atropaic acid is treated with hydrobromic acid in the same manner as cinnamic acid, *bromhydratropaic acid* is obtained in very impure condition, although the crude product contains very nearly the theoretical percentage of bromine. The purification of the acid presents some difficulty. The concentrated solutions of the acid in carbon disulphide, benzol or chloroform, are thick syrups, which deposit crystals with difficulty. The acid is less soluble in water-free ligroin (b. pt., below 100°). By slow diffusion of ligroin into the carbon disulphide solution, the acid is obtained in large colorless, apparently triklinic crystals, which are insoluble in water; m. pt. 93–94°.

The acid is a little more stable than the isomeric bromhydrocinnamic acid. Cold sodium carbonate dissolves it without decomposition, which, however, takes place rapidly if the solution is heated. Only a trace of atropaic acid is produced, and not a trace of hydrocarbon (difference from the cinnamic acid derivative). The principal product is an acid, designated as *atrolactic* acid, altogether

different from tropaic acid. Atrolactic acid,* $C_9H_{10}O_3 + \frac{1}{2} H_2O$; water of crystallisation escapes between 80 and 85°; m. pt. of the dehydrated acid 93–94°. The acid dissolves readily in cold water; in all proportions in hot water. The lime salt $(C_9H_9O_3)_2 Ca + 8H_2O$, easily soluble in hot water, more difficultly in cold water. The barium salt, with $2H_2O$, and zinc salt, with $2H_2O$, are difficultly soluble in water. The same products were obtained by boiling bromhydratropaic acid with water; in this case atropaic acid is produced in considerable quantity. Bromhydratropaic acid dissolves in cold concentrated ammonia without decomposition. The solution is decomposed on standing, yielding amidohydratropaic acid, atrolactic acid and atropaic acid. *Amidohydratropaic acid*, $C_9H_{11}NO_2$, beautiful glistening scales; m. pt. 169.5°; difficultly soluble in cold water, very easily in hot water.

Dibromhydratropaic acid, $C_9H_8Br_2O_2$.—Atropaic acid combines with bromine as easily as cinnamic acid. The yield of dibromhydratropaic acid is very nearly theoretical. The acid dissolves readily in boiling carbon disulphide, pretty difficultly in the cold, and crystallizes in long silken needles; m. pt. 115–116°; decomposition at 140°. The acid dissolves easily in boiling chloroform, more difficultly in ligroin. The acid is decomposed on boiling with water, $C_9H_8Br_2O_2 + H_2O =$ C_8H_8O (acetophenon) $CO_2 + 2$ HBr, being the principal, if not the only reaction. The same decomposition takes place in the alkaline solution in the cold. *Acetophenon*, $C_6H_5 - CO - CH_3$, m. pt. betw. 16.5–18°, b. pt. 202°, was further identified by direct comparison of its dibromide and the dibromacetophenon, ($C_6H_5 - CO - CHBr_2$, described by Hunnius) prepared from commercial acetophenon. If dibromhydratropaic acid is heated with less water to 100° in sealed tubes, acetophenon is obtained as principal product, and *monobromatropaic acid*, $C_9H_7BrO_2$, as byproduct. This acid dissolves with difficulty in cold water, more readily in hot water. The aqueous solution yields it in needles. Chloroform and ligroin, in which it dissolves readily, especially on heating, furnish it in small well developed crystals; m. pt. 130°. The acid is not decomposed in aqueous or alkaline solution on boiling. It combines with bromine to *tribromhydratropaic acid*, $C_6H_5.C_2HBr_3.CO_2H$, m. pt. 150°; easily soluble in carbon disulphide or chloroform, less so in ligroin.

Atropaic acid combines readily with hydrogen to *hydratropaic acid*, b. pt. 264–265°, colorless heavy oil, very little soluble in water,

* Fittig calls attention to the great similarity between this acid and Glaser's phenyllactic acid, suggesting that they may be identical.

more volatile with water vapor than atropaic acid. The calcium salt crystallizes with 2 or 3 H_2O.

Dibromhydratropaic acid yields hydratropaic acid and atrolactic acid, on treatment with nascent hydrogen.

The results given lead to the formula $C_6H_5 - C\begin{cases}CH_2\\COOH\end{cases}$ for atropaic acid, and the probable formulæ of the derivatives $C_6H_5 - CH\begin{cases}CH_3\\COOH\end{cases}$ hydratropaic; $C_6H_5 - CH\begin{cases}CH_2Br,\\COOH\end{cases}$ bromhydratropaic acid; $C_6H_5.CBr\begin{cases}CH_2Br\\COOH\end{cases}$ dibromatropaic; $C_6H_5.CH\begin{cases}CH_2OH*\\COOH\end{cases}$ atrolactic; $C_6H_5.C(OH)\begin{cases}CH_3\\COOH\end{cases}$ tropaic; $C_6H_5.CH\begin{cases}CH_2NH_2\\COOH\end{cases}$ amidohydratropaic acid.

Isatropaic acid does not yield addition products, and is probably a polymerisation product of atropaic acid.

4. *Formation of Non-saturated Hydrocarbons from the Addition Products of the Non-saturated Acids*, R. FITTIG (pp. 169–179).—The author concludes from the facts stated in the foregoing papers, that the hydrobromic addition products of the non-saturated acids, which yield hydrocarbons on neutralization with sodium carbonate, contain the Br atom and COOH group in combination with the same carbon atom. The formulæ arrived at by Perkin † for the higher homologues of cinnamic acid do not conform to this theory. The author believes that further investigation will modify these formulæ in accordance with his own theory. Perkin denies the importance of the metal atom, which the author, however, considers essential in the reaction. $CH_3 - CH_2 - CBr\begin{cases}CH_3\\COONa\end{cases} = CH_3 - CH_2 - \underset{\|}{C} - CH_3 + NaBr + CO_2$, an unsaturated hydrocarbon being formed at first, which, however, does not necessarily remain so: $CH_3 - CH_2 - \underset{\|}{C} - CH_3 = CH_3 - CH = CH - CH_3$ (pseudobutylene). In the same manner he explains the formation of acetophenon from dibromhydratropaic acid. $C_6H_5 - CBr\begin{cases}CH_2Br\\COOH\end{cases} + H_2O = C_6H_5 - C\begin{cases}CH_2OH\\\end{cases} + NaBr$ and $C_6H_5 - C\begin{cases}CH_2OH\\\end{cases} = C_6H_5 - C\begin{cases}CH_3\\O\end{cases}$.

The Halogen Substitution Products of Ethane. First paper. WILH. STAEDEL (Ann. Chem., **195**, 180–205).—1. Action of chlorine on ethylchloride. Kraemer describes ethylenechloride among the

* Under the supposition that it is not phenyllactic acid.

† Jour. Chem. Soc., 1877, ii, 660

byproducts in the manufacture of chloral, and explains its formation by the action of chlorine on ethylchloride. Geuther mentions ethylenechloride (b. pt. 84°) among the various products of the action of chlorine on ethylchloride. These two statements induced the author to resume his own experimeuts, undertaken some two years ago, on very considerable quantities of material. The results obtained were the same as before,* that ethylenechloride was not formed in the reaction, that ethylidenechloride, $H_3C.CHCl_2$, was the only bichloride formed.—2. Action of chlorine on ethylidenechloride (b. pt. 59°) yielded the two possible trichlorides. Dichlorethylchloride $H_3C.CCl_3$, b. pt. 74–75°. Monochlorethylenechloride, $H_2ClC.CHCl_2$, b. pt. 114–115°, already described by Regnault and Geuther as among the products of the reaction of chlorine on ethylchloride.—3. Action of chlorine on ethylenechloride. Dichlorethylchloride does not form in the reaction. Monochlorethylenechloride, b. pt. 115°, is the only trichloride produced (Regnault).—4. Chlorine and dichlorethylchloride (b. pt. 74–75°) yield trichlorethylchloride, $H_2ClC.CCl_3$, b. pt. 127.5°. Geuther's dichlorethylenechloride (b. pt. 133–136°) was evidently a mixture of two isomeres, $C_2H_2Cl_4$, having been prepared from a mixture of trichlorides.—5. Chlorine and monochlorethylenechloride. Products of constant boiling points, could not be obtained (115–180°), from which the author infers that both tetrachlorides possible had formed; trichlorethylchloride, b. pt. 127.5°, and dichlorethylenechloride, b. pt. 147°.—6. Pentachlorethane and hexachlorine. The author refers to the preliminary communication by himself and E. Hahn in the Ber. d. d. ch. Ges.—7. Chorbrom substitution products of ethane. Julius Denzel. By prolonged action of direct sunlight on mixtures of equal molecules of bromine and ethyl chloride, colorless liquids were obtained, which distilled between 50 and 205°. By fractional distillation, four bodies were isolated.—*a.* α chlorbromethane, $H_3C.CHBrCl$, b. pt. 84–85.5° (uncorr.), liquid at—20°, sp. g.=1.667 at 16°, is attacked very slowly by alcoholic potash solution at ordinary temperature. β chlorbromethane, b. pt. 105–108°, which is rapidly attacked by alcoholic potash, was not among the products of the reaction.—*b.* α chlordibromethane, $H_3C.CBr_2Cl$, colorless liquid, b. pt. 123–124° (uncorr.), liquid at—20°, sp. g.=2.134 (16°), odor reminds of oil of turpentine; alcoholic potash acts upon it after 15 minutes standing.—*c.* β chlordibromethane, $BrH_2C.CHBrCl$, liquid at—20°, b. pt. 162.5–163°; sp. g.=2.268 (16°); alcoholic potash acts upon it at once.—*d.* α chlortribromethane, $HBr_2C.CBr_2Cl$, liquid at—20°, b. pt. 200–201° (uncorr.), sp. g.=2.602 at

* Zschft. f. Ch., 1871, 197.

16°. The same product was obtained on treatment of α or β chlordibromethane with bromine in direct sunlight; besides this, α chlortetrabromethane, $HBr_2C—CBr_2Cl$, m. pt. 32–33°, b. pt. 240°(?), sp. g.= 3.366 (16°), had also formed in the reaction.

By the action in direct sunlight of equal molecules of bromine and ethylidenechloride upon each other, three derivatives were obtained.—*a.* α dichlorbromethane, $H_3C.CBrCl_2$, liquid at—20°, b. pt. 98–99° (unc.), sp. g.=1.752 at 16°; at ordinary temperature, alcoholic potash attacks it very slowly.—*b.* α dichlordibromethane, $H_2BrC.CBrCl_2$, liquid at—20°, b. pt. 176-178°, sp. g.=2.27.—*c.* α dichlortribromethane, $HBr_2C.CBrCl_2$, oily liquid, even at—20°, b. pt. 215–220°.—8. Bromine substitution products of ethane, Jul. Denzel. Action of 1 mol bromethyl and 2 mol bromine in direct sunlight, yielded ethylidenebromide (α dibromethane), b. pt. 109–110°, and α tribromethane, b. pt. 187–188°. Ethylene bromide (β dibromethane) could not be found among the products of the reaction. The author is still engaged in the examination of the products obtained by the further action of bromine. —9. Experiments with regard to the substituting action of iodine on chlorbromethane, in sunlight, yielded negative results.

The facts thus given are considered of interest in the solution of the question of the influence of the constitution and the character of the constituents of a derivative on the course of the substitution of hydrogen in said derivative.

Chlorbrom and Bromine Substitution Products of Ethylene, JULIUS DENZEL (Ann. Chem., **195**, 205–210).—α chlorbromethylene, $H_2C=CBrCl$, obtained by the action of alcoholic potash on α or β chlordibromethane, colorless liquid (b. pt. 62–63°), which rapidly changes into an amorphous white body by polymerisation.—α chlordibromethylene, $HBrC=CBrCl$, obtained by action of alcoholic potash on α chlortribromethane, liquid at—20°, sp. g.=2.275, b. pt. 141-142°.—α dichlorbromethylene, $HBrC=CCl_2$, obtained from α dichlordibromethane, liquid at—20°, sp. g.=1.906 (16°). Dichlordibromethylene (b. pt. 194°?), quantity obtained too small for thorough examination. Of the bromine substitution products, which the author did not prepare, only the different statements in regard to the boiling points are given.

Nomenclature and Boiling Points of the Chlorbrom and Bromine Substitution Products of Ethane and Ethylene,* JULIUS DENZEL (Ann. Chem., **195**, 210–218).—The terms of ethane, ethylene and acetylene are limited to the derivatives bearing the

* Exclusive of isomeres, which would follow from the assumption of asymetric carbon atoms.

character of these hydrocarbons, expressed in the bond of the carbon atoms. The isomeres are distinguished by letters or numbers. The substituting elements or groups are placed one after the other in the order of their affinity, beginning with the strongest or determining affinity. Thus:

Chlorbromethanes: $H_3C - \underset{\alpha}{CHBrCl}$; $H_2BrC - \underset{\beta}{CH_2Cl}$.

Chlordibromethanes: $H_3C - \underset{\alpha}{CBr_2Cl}$; $H_2BrC - \underset{\beta}{CHBrCl}$;
$HBr_2C - \underset{\gamma}{CH_2Cl}$.

Chlorbromiodoethanes: $H_3C - \underset{\alpha}{CIBrCl}$; $H_2IC - \underset{\beta}{CHBrCl}$;
$H_2BrC - \underset{\gamma}{CHICl}$; $HBrIC - \underset{\delta}{CH_2Cl}$.

The 1 or α modifications contain the substituting atoms or groups as much as possible in combination with the same carbon atom; 2 or β, containing the second strongest affinity next to the determining affinity; 3 or γ, with the third strongest affinity next to the determining; modification 4 or δ, in which the determining affinity is isolated as much as possible from the others.

Regularities in the boiling points are perceptible as follows:

α Chlorethane, $H_3C.CH_2Cl$;	b. pt. 12°		
α Chlorbromethane, $H_3C.CHBrCl$;	" 85°	diff.	73°
α Chlordibromethane, $H_3C.CBr_2Cl$;	" 124°	"	39°
α Chlortribromethane, $H_2BrC.CBr_2Cl$;	" 201°	"	77°
α Chlortetrabromethane, $HBr_2C.CBr_2Cl$;	" 240°	"	39°

α Chlorbromethane, b. pt.	85°	α Chlordibromethane, b. pt. 124°	diff. 39°
β " "	105° diff. 20°	β " "	163° etc.

In the original this table is further extended to the comparison of the dichlorethane derivatives, the bromethanes and the ethylene derivatives. Differences of about 80, 40 and 20 occur repeatedly. In the chlorbrom substitution products each bromine atom entering raises the b. pt. by about 40°, when it attaches itself to a carbon atom already in combination with hydrogen, otherwise by 80° (the first member of the above series forms an exception to this rule). The boiling point is raised by about 25° in the exchange of a chlorine atom for a bromine atom:

C_2H_5Cl,	b. pt. 12°		$H_3C - CHCl_2$,	b. pt. 58°	
C_2H_5Br.	" 39°	diff. 27°	$H_3C - CHBrCl$	" 85°	diff. 27°

$H_3C.CCl_3$	b. pt. 75°	
$H_3C.CBrCl_2$	" 99°	diff. 24°

etc. The derivatives of CH_4 and SiH_4 show the same regularities.

Simple Apparatus for the Regulation and Variation of Pressure in Distillations, Determinations of Boiling Points, etc., WILH. STAEDEL and E. HAHN (Ann. Chem., **195**, 218–221). Not intelligible without the plates appended to the original.

Reduction of Analytical Weighings to a Vacuum, G. F. BECKER (Ann. Chem., **195**, 222–227).—The author gives tables of corrections for platinum and brass weights derived from the following equations: $w_{,} = w + \frac{wc}{y} - \frac{wc}{d}$, wherein $w_{,}$ represents the real weight, w the apparent weight and y the sp. gr. of the substance weighed, d the sp. gr. of the weights, c the weight of 1 cc air. $x = w_{,} - w$; x represents the correction. If $w_{,} = 1$ gm, $x = \frac{c}{y} - \frac{c}{d}$. The equation $\frac{dy}{dx} = -\frac{y^2}{c}$ represents the influence of the sp. gr. of the substance of the weights on the corrections. The influence of temperature is expressed in $x_{,} = c_0 (t \times 0.00366) (\frac{1}{y} - \frac{1}{d})$. In the present state of chemical apparatus, the influence of barometric pressure is inappreciable.

Hydrogen Peroxide. Third paper. EM. SCHOENE (Ann. Chem., **195**, 228–252).—Behavior of pure *hydrogen peroxide* towards neutral *potassium iodide*. The paper begins with a review of the statements of Schoenbein, Meissner, Al. Schmidt, Weltzien, Houzeau, H. Struve and O. Loew. By a series of very careful quantitative and qualitative experiments the author arrives at the following results :

1. Pure hydrogen peroxide (vapor or in aqueous solution) separates iodine from potassium iodide. 2. Caustic potash is formed in the reaction. 3. The more dilute the solutions are, the later the reaction begins, and the more slowly it takes place.* 4. The reaction proceeds gradually, not suddenly, as in the presence of ferrous sulphate. 5. The reaction is accompanied by the evolution of oxygen. 6. More concentrated solutions (containing more than 0.2 p. c. H_2O_2) give the same intensity of iodine coloration as more dilute solutions (0.002 p. c. H_2O_2). Only when the amounts of hydrogen peroxide are smaller than 10 mgs to 1 ltr, appreciable differences in intensity of coloration are noticeable.

* Iodide of potassium and starch form a very delicate test for peroxide of hydrogen, as little as 8 one hundred-millionth part in solution being recognizable.

The action of the potassium iodide on hydrogen peroxide is katalytic. Potassium iodide causes the decomposition of the hydrogen peroxide into water and oxygen, and but a small proportion of the iodide itself is decomposed. The author explains this reaction by the following equations: (1.) $2KI + 2H_2O = 2KOH + 2HI$ (amount of dissociation depending on concentration). (2_1.) $H_2O_2 + 2KOH = K_2O_2 + 2H_2O$ and (2_2.) $H_2O_2 + 2HI = I_2 + 2H_2O$. (3.) $K_2O_2 + I_2 = 2KI + O_2$. The regenerated potassium iodide acts again in the same manner. With increasing dilution the katalytic decomposition is less energetic and complete. If the quantity of water is considerable the reactions (2_1.) and (2_2.) will take place in a minor degree and more slowly.

The author offers the same explanation for the katalytic decomposition of hydrogen peroxide by concentrated solutions of the halcid salts of the metals of alkalies and alkaline earths.

Hexylenes from the Tertiary Hexyl Alcohols and their Polymerisation Products. L. JAWEIN (Ann. Chem., **195**, 253–264).—Hexylene from dimethylpropylcarbinol. The alcohol (b. pt. 122.5–123.5°) was prepared by the action of 1 mol chlorbutyryl on 2 mol zincmethyl. Yield only small, as the hexyl alcohol splits up very largely into hexylene and water. The hexylene thus obtained, and the hexylene obtained from the iodide (prepared from the alcohol), are identical. The hexylene boils at 65–67°, sp. g. 1.372 (0°). It combines with hydroiodic acid to hexyl iodide (b. pt. tolerably constant at 142°); with bromine it yields a bromide which cannot be distilled without decomposition. On oxidation with chromic acid, this hexylene yields aceton (b. pt. 57–58°), a keton that distils at 115°, acetic and propionic acids; hence the formula $(CH_3)_2C{=}CHC_2H_5$. The hydrocarbon is polymerised on treatment with dilute sulphuric acid [more than 2 vol dilute acid (2 pts. H_2SO_4 to 1 pt H_2O) to 1 vol of hexylene] yielding dihexylene, b. pt. 193–197°, sp. g. 0.797 (0°), vapor density 5.88 (calc. 5.81).—Hexylene from diethylmethylcarbinol, has been already obtained by Tschaikowsky. Diethylmethylcarbinol, b. pt. 121–122.5° (758 mm), yields hexylene with b. pt. 69.5–71°, sp. g. 0.712 (0°). On oxidation with chromic acid, this hexylene yields acetic acid and a mixture of ketones, the larger portion of which distils between 80–86° (methylethylketon ?), the remainder at 86–123°. Hence the formula $CH_3HC{=}C.CH_3.C_2H_5$. The dihexylene boils at 196–199°, sp. g. 0.809 at 0°, vapor density 5.97 (calc. 5.81).

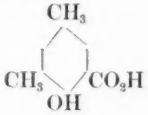
Upon the Products of the Fusion of Potassium Mesitylene Sulphate with Potassium Hydrate, OSCAR JACOBSEN (Ann. Chem., **195**, 265–292).—The author finds that mesitol is the first product of the reaction. On fusion with potassium hydrate, pure mesitol yields oximesitylenic acid; pure oximesitylenic acid yields an oxiuvitic acid, which by the further action of fused potassium hydrate, is finally, though very slowly, oxidized to trimesic acid. Hence potassium mesitylene sulphate yields all these products on fusion with potassium hydrate, if the reaction is continued for a sufficient length of time. These results would rectify the statement of Fittig and Hoogewerff,* and verify in part the results of Biedermann and Ledoux.† Fittig and Hoogewerff had assumed that oximesitylenic acid was the first product of the reaction. They considered the phenol, which they mistook for xylenol, as secondarily derived from the former by the loss of carbonic acid. Biedermann and Ledoux obtained mesitol and oximesitylenic (?) acid.

The formation of mesitol potassium from the mesitylene sulphate takes place slowly much below the fusing point of mesitol potassium, but at this lower temperature, while it forms, it is at once oxidized to oxi-acids. If, however, a considerably higher degree of heat is applied, the now rapidly forming mesitol potassium melts and rises to the surface, being altogether insoluble in the fused potassium hydrate, thus escaping further oxidation. For this reason, at lower temperature oxi-acids are principally formed, while the reaction at higher temperature produces mainly mesitol.

Mesitol, $C_6H_2(CH_3)_3OH$, m. pt. 68°, b. pt. 219.5° (763 mm), very volatile with water vapor, sublimes below the melting point in fine needles, little soluble in water, very easily in alcohol or ether. The solutions are not colored by ferric chloride. With concentrated sulphuric acid it yields mesitolsulphonic acid, the sodium and barium salts of which are extremely soluble in water, and in solution give an intense blue coloration with ferric chloride.—Monobrommesitol, m. pt. 80° (Biedermann and Ledoux).—Dibrommesitol, m. pt. 150°, not volatile without decomposition, slightly soluble in hot water, more readily in warm solutions of the alkaline carbonates. In its preparation water must be altogether excluded. In the presence of water, $C_8H_6O_2Br_2$ (?), dibrommetaxylolquinon is among the products formed, which is identical with the body described by Fittig and Hoogewerff as dibromxylenol. It crystallizes from alcohol in large, gold-colored plates, insoluble in water and the alkaline carbonates, m. pt. 176°.

* Ann. Chem., **150**, 333.
† Ber. d. d. ch. Ges., viii, 250.

Oximesitylenic acid, m. pt. 179°, agreed with the description given of it by Fittig and Hoogewerff.—Commercial acetonmesitylene contains metaxylol; the oximesitylenic acid obtained from it contains oxitoluic acids, if the mesitylene sulphate has not been very carefully purified. To the latter impurity the author ascribes the discrepancy between the results of Ledoux and Biedermann, and Fittig and Hoogewerff, regarding this acid.—Oximesitylenic acid is also obtained at lower temperature, on fusion of mesitol sulphate with potassium hydrate; a dioximesitylenic acid does not seem to form in the reaction. Salts of oximesitylenic acid: $(C_9H_9O_3)_2$, Ba + $5H_2O$, only moderately soluble in cold water, loses its water of crystallization below 100°, becomes yellow at 110° and gray at 140–150°, by oxidation; calcium salt with 4 H_2O, easily soluble; zinc salt with 2 H_2O, less soluble in hot than in cold water; copper salt difficultly soluble; potassium and ammonium salts without water of crystallization.—Methyl ether, colorless oily liquid, easily volatile with water vapor. When heated with concentrated hydrochloric acid to 200–205°, oximesitylenic acid yields metaxylenol (1.3.4.); hence the constitution



Oxiuvitic acid, $C_6H_2.CH_3.OH.(COOH)_2$, colorless needles, much more soluble in hot than in cold water. Solutions give a cherry-red coloration with ferric chloride. When slowly heated the acid melts gradually between 225–235°. If somewhat larger quantities are rapidly heated, fusion takes place suddenly at 275°. The barium, calcium, magnesium and sodium salts are very soluble in water. Calcium salt very difficultly soluble in cold water, pretty easily in hot water. Dimethyl ether, m. pt. 79°, long needles, very volatile with water vapor. When heated with concentrated hydrochloric acid to 200°, the acid yielded orthokresol; hence the constitution $C_6H_2.\overset{1}{C}O_2H.\overset{3}{C}O_2H.\overset{4}{O}H.\overset{5}{C}H_3$. Among the products of the reaction there was besides orthokresol, a coloring matter which dissolved in dilute sodium carbonate solution to an intensely purple liquid. This substance was obtained from the alcoholic solution in crystals with greenish reflection.

In the same manner as mesitylene, ethyldimethylbenzol yields a monobasic oxi-acid (m. pt. 147–149°), volatile with

water vapor, which gives a blue coloration with ferric chloride, and to which the formula $C_6H_2.\overset{1}{C_2H_5}.\overset{3}{CO_2H}.\overset{4}{OH}.\overset{3}{CH}$ will probably have to be assigned.

Analysis of Organic Compounds Containing Halogens or Nitrogen, HUGO SCHIFF (Ann. Chem., **195**, 294–302).

Molecular Weight of Indigo, ERWIN V. SOMMARUGA (Ann. Chem., **195**, 301–313).—Averaging the results of nine determinations, made by a modification of the method Dumas-Habermann, the author has found the vapor density of indigotin at 9.45 (air = 1). Hence the molecule of indigo, $C_{16}H_{10}N_2O_2$, calculated vapor density 9.06. The results obtained by the method of V. Meyer were lower, varying from 7.37–8.26, in consequence of the decomposition of part of the indigo. The indigotin employed in the determinations had been purified by the method of Fritsche (Journ. pr. Ch., **28**, 139) and subsequent sublimation at a pressure of between 30–40 mm.

Detection of so-called Ethyldiacetic Acid in Urine, A. HILGER (Ann. Chem., **195**, 314–317).—The urine in an interesting case of diabetes mellitus was found to contain ethyldiacetic acid. With ferric chloride it gave the characteristic dark cherry-red coloration. The detection of the acid was based upon the fact determined by Geuther, that, by addition of water, the acid is decomposed into aceton, alcohol and carbonic acid; 300 cc of urine were distilled with 50–60 cc concentrated HCl, to one-third. The distillate showed very decided aceton odor; after the addition of potassium hydrate and an excess of iodine solution, upon standing, it yielded the characteristic iodoform crystals. The distillate was subjected to careful fractional distillation. The portion which passed over below 56° contained aceton, which was identified by the formic acid obtained on careful oxidation with chromic acid mixture. The portion distilling above 56° does not show aceton acid, gives an ample iodoform reaction, and yields acetic and carbonic acid on oxidation with chromic acid. Attempts to prepare the acid from the urine by the method of Rupstein* proved unsuccessful. An approximate quantitative determination of the acid was effected by the quantitative determination of the iodoform obtained from the acid, assuming that 3 mol CI_3H correspond to 1 mol acid. 60.80, or 100 cc of the urine, were strongly acidulated with hydrochloric acid and distilled to one-third. To the distillate potassium hydrate and an excess of a concentrated solution of iodine in potassium iodide

* Centrbl. f. med. Wiss., 1874, No. 55.

were at once added; the mixture was then slightly warmed and allowed to stand in a closed vessel for twenty-four hours. The iodoform obtained was weighed, after washing with cold water, and drying at ordinary temperature and over sulphuric acid. The quantities of the acid in the urine were found to vary between 0.0985–0.1909 in 100 pts. Aceton and alcohol could be also detected in the condensation products of the air exhaled by the patient.

Solanine and its Decomposition Products. A. HILGER (Ann. Chem., **195**, 317–325).—The solanine (m. pt. 235°) analyzed, had been recrystallized from alcohol and dried at 100°. From the results of his analysis the author calculates the formula $C_{42}H_{87}NO_{15}$. The acetyl compound, obtained by heating 2 parts solanine with 10 parts acetic anhydride for several hours to 160°, is insoluble in water, soluble in alcohol and ether, crystallizes in long needles, and contains 23 p. c. acetyl, corresponding, according to the calculation of the author, to 6 acetyl rests, or the formula $C_{42}H_{69}(C_2H_3O_6)NO_{15}$.

On boiling with dilute hydrochloric acid, solanine yielded 36 p. c. sugar (determined as glucose by Fehling's solution) and solanidine. (Dilute sulphuric acid yielded 35.7 p. c. sugar.)

Solanidine (m. pt. 208°) had been recrystallized from ether. $C_{26}H_{41}NO_2$, the formula derived by the author from his analyses. The acetyl compound of solanidine yielded 35.4 p. c. acetyl, corresponding to 5 acetyl rests, or the formula $C_{26}H_{36}(C_2H_3O)_5NO_2$.

An equation, explaining the decomposition of solanine, cannot be derived from the quantities of sugar found and the formulæ given for solanine and solanidine.

Potassium hydrate, in solution or fused, does not act upon solanine.

Several New Uranyl Salts. R. SENDTNER (Ann. Chem., **195**, 325–333). *Selenates.*—$(UO_2)SeO_4 + SeO_4H_2 + 18aq$, light yellow masses of wavellite structure, deliquescent. $2(UO_2SeO_4)SeO_4H_2 + 12H_2O$ (?), greenish-yellow, efflorescent needles.

These salts were obtained by dissolving uranic hydrate in a dilute solution of selenic acid, and subsequent concentration. The saturated solution of uranic hydrate in selenic acid yielded, on evaporation to dryness, a varnish-like mass $UO_2SO_4 + xH_2O$.— $SeO_4(UO_2)SeO_2K_2 + 2H_2O$, granular crusts, obtained by dissolving potassium uranate in selenic acid. The salt dissolves easily in hot water, less so in cold water. $SeO_4(UO_2)\ SeO_4(NH_4)_2 + 2H_2O$, readily soluble in water.

Selenites.—$SeO_3(UO_2)SeO_3H_2$, yellow microscopic prisms, insoluble in water, obtained in small quantity by solution of uranic hydrate in

selenious acid, in more considerable quantity by boiling the mixed concentrated aqueous solutions of uranyl chloride and selenious acid. $SeO_3(UO_2)SeO_3K_2$, pale yellow crusts, insoluble in water. Ammonium double salt, microscopic plates, insoluble in water.

The author did not succeed in obtaining the iodide corresponding to uranyl chloride, or the uranyl iodide double compounds with potassium or ammonium iodide. Attempts to obtain uranous bromide in a manner analogous to the preparation of the chloride were likewise unsuccessful. $(UO_2)Br_2 + 7H_2O$, granular deliquescent mass. $(UO_2)Br_2 + 2KBr + 2H_2O$, yellowish-brown rhombic plates, very soluble in water. $(UO_2)Br_2 + 2(NH_4)Br + 2H_2O$, large rhombic plates. The two latter salts are decomposed by water in the same manner as the corresponding chlorides; they can be obtained in crystals from the solutions only in the presence of an excess of acid.

Upon the Influence of the Isomerism of the Alcohols and Acids in the Formation of Compound Ethers, N. MENSCHUTKIN (Ann. Chem., **195**, 334–364).—The pure water-free alcohols and and acids were weighed out and mixed as nearly as possible in the ratio of the molecular weights. Weighed portions of these mixtures were heated in small sealed tubes from 1 to 300 hours, at a perfectly constant temperature of 154°. The degree of etherisation was determined by dissolving the reaction products thus obtained in dilute alcohol, and titrating the unetherified acid with baryta water, using rosolic acid as an indicator. The method yields perfectly constant results.

In the manner indicated, the author determined with extreme care, the velocities and limits of the acetic acid etherification of the following alcohols: 1. Primary saturated alcohols—methyl alcohol, ethyl alcohol, propyl alcohol, normal butyl alcohol, isobutyl alcohol, normal octyl alcohol and cetyl alcohol. 2. Primary non-saturated alcohols—allyl alcohol and benzyl alcohol.

Berthelot and Péan de St. Gilles inferred from their experiments that the velocities of etherification of the primary alcohols were equal, and further, that the limit of etherification increased with the increase of the molecular weight. The author defines as absolute velocity the percentage of acid (or alcohol) etherified, with reference to the total quantity of acid or alcohol employed; as relative velocity, the percentage of etherified acid (or alcohol) with reference to the quantity of acid (or alcohol) at all capable of etherification (this latter quantity is determined in the limit of etherification); as initial velocity, the velocity of etherification in the action of molecular

quantities of alcohol and acid at 154°, at the end of the first hour. His results may be comprised as follows: 1. Methyl alcohol shows the greatest velocity; its position of all alcohols is an exceptional one. Absolute initial velocity of the methylacetic system, 55.59 p. c.; relative initial velocity, 80.8. 2*a*. The absolute initial velocities of the normal primary alcohols are equal, amounting to about 47 p. c.

Ethyl alcohol, 46.81; propyl alcohol, 46.50;
Normal butyl alcohol, 46.85; octyl alcohol, 46.57.

In the further course of etherification the velocities of etherification of ethyl, propyl and normal butyl alcohol are about equal; the velocity of octyl alcohol is decidedly greater (in this case the system is, however, not homogeneous). *b*. Influence of isomerism:

Absolute initial velocity of isobutyl alcohol, 44.92.
" " " " normal butyl alcohol, 46.85.

Although the initial velocity of isobutyl alcohol is smaller than that of the normal alcohol, the velocity is greater in the succeeding hours.

3*a*. The relative initial velocity of alcohols of the same structure decreases with an increase of the molecular weight.

Ethyl alcohol, 70.31; propyl alcohol, 69.55;
Normal butyl alcohol, 69.61; octyl alcohol, 64.39.

b. Influence of isomerism:

Relative initial velocity of normal butyl alcohol, 69.61.
" " " " isobutyl alcohol, 66.66.

4. Influence of the composition:

Absolute initial velocity: allyl alcohol, 36.12; benzyl alcohol, 37.98.

The absolute initial velocities of the non-saturated primary alcohols are much smaller than those of the saturated primary alcohols.

Relative initial velocity: Allyl alcohol, 60.07; benzyl alcohol, 62.52.

5. Limits of acetic systems of primary alcohols. The following limits were derived by taking the mean of experiments of 120 hours:

Methyl alcohol.....69.59	Isobutyl alcohol.....67.38
Ethyl alcohol.....66.57	Octyl alcohol.....72.34
Propyl alcohol.....66.85	Cetyl alcohol.....80.39
Normal butyl alcohol....67.30	Allyl alcohol.....59.41

Benzyl alcohol.....60.75

Methyl alcohol differs again from the rest of the alcohols. As to the other alcohols, the limits increase with the increase of the molecular weight. Isomerism of the alcohols does not seem to influence the limit, as will be seen by comparison of the limits of the two butyl alcohols.

The composition greatly affects the limit of etherification, as will be seen by comparison of the saturated and non-saturated alcohols.

Contributions to the Knowledge of Polyporic Acid, C. STAHLSCHMIDT (Ann. Chem., **195**, 365–372).—Polyporic acid (Ann. Chem., **187**, 177), the acid discovered by the author in polyporus purpurascens, is decomposed on boiling with moderately concentrated potash solution. The original purple color of the solution disappears, and the nearly colorless liquid obtained, yields, upon supersaturation with dilute sulphuric acid, a white precipitate which is a mixture of two acid compounds. Hydropolyporic acid, which constitutes the main portion of this precipitate, crystallizes in white needles, is readily soluble in hot water and alcohol, and has the composition $C_9H_9O_2$. It fuses at 162°, and sublimes, when cautiously heated. The other compound, $C_{10}H_9O$, is altogether insoluble in water, dissolves readily in boiling spirits, fuses at 156° C., and sublimes without decomposition.

The following salts of hydropolyporic acid are described: $C_9H_8NaO_2 + 2H_2O$, colorless prisms, which are very easily soluble in water; $(C_9H_8O_2)_2Ba$, quadratic plates, difficultly soluble in water; $(C_9H_8O_2)_2Mn + 3H_2O$, very difficultly soluble in water; copper salt, a light blue crystalline precipitate; cobalt salt, white crystalline precipitate; lead salt, amorphous white precipitate; $C_9H_8O_2Ag$, white crystalline precipitate. The methyl ether was obtained in crystals; the ethyl ether as an oily liquid.

Polyporic acid is acted upon by warm concentrated nitric acid, yielding nitropolyporic acid, $C_9H_6O_2(NO_2)$ (m. pt. 230°, little soluble in cold water, easily soluble in hot water and alcohol) and benzoic acid. A small quantity of picric acid is also formed in the reaction.

By the action of hydrochloric acid and potassium chlorate on polyporic acid, a mixture of three chlorine compounds is obtained. $C_9H_7Cl_2O_2$ (?) dissolves in boiling water, white feathery needles, m. pt. 108°; the compound sublimes in white needles at a still higher temperature. $C_8H_6Cl_2O$, long gold colored needles, which are insoluble in water, but very easily soluble in boiling alcohol. The compound fuses at 109–110°, and sublimes at still higher temperature without decomposition.

The third chlorine compound, insoluble in water, easily soluble in boiling alcohol, forms a syruppy mass, and could not be obtained pure.

Bromine acts upon polyporic acid; crystallized compounds, however, could not be obtained.

Contributions to the Knowledge of the Ammoniacal Mercury Compounds, H. GERRESHEIM (Ann. Chem., **195**, 373–386).—Millon's base, the yellow compound formed in the action of ammonia on precipitated HgO, according to the analysis of the author, corresponds to the formula $Hg_{11}O_3N_2H_4 + 2H_2O$. It is insoluble in alcohol, ether and all solvents, which do not act upon it chemically; it is slightly soluble in water. The hot concentrated aqueous solution yields it in microscopic crystals. When heated in a dry current of air it loses one-third of the total nitrogen in the form of ammonia, and $3H_2O$. Potash solution does not act upon it, even on boiling. On evaporation with potash the base is converted into a brown substance (ammonia escapes). Nitric acid converts the base into a white nitrate, insoluble in nitric acid. Hydrochloric acid yields white chloride, soluble under decomposition in an excess of the acid. Dilute sulphuric acid yields a white salt, insoluble in an excess of the acid. Concentrated acid turns it brown by dehydration; on heating, sulphurous acid is evolved. The acetic acid salt is soluble in an excess of acetic acid. From this solution nitric acid precipitates the nitrate, sulphuric acid the sulphate, etc.

The salts of the base, which are difficultly soluble in dilute acetic acid, are precipitated by addition of the corresponding salts to this solution. The salts thus obtained are white, or yellowish-white, if the acid does not possess individual color. The permanganate is red; the chromate, yellow.

The base, if employed in excess, withdraws the acid completely from all soluble salts and many insoluble salts, without being dissolved itself. On shaking a solution of potassium chloride with the base, a filtrate is obtained which contains only potassium hydrate, not a trace of chlorine. Sulphate of sodium, nitrate of potassium are decomposed in corresponding manner. Even sulphate of barium, on standing with the base and filtering, yields a filtrate containing notable quantities of caustic baryta.

The base, on treatment with iodide of ethyl, at 100°, yields a double salt, $2(C_2H_5)_4NI + 3HgI_2$, m. pt. 153–154°. Bromethyl yields the corresponding bromine compound (m. pt. 147–150°). In the action of chloroform on the base, a gaseous compound is formed, besides the chloride and formate of the base, and mercuric cyanide and

ammonia. Carbon disulphide yields brownish-black sulphocarbonate.

The author has also utilized the insolubility of the ammoniacal mercury compound in the quantitative determination of ammonia. If sodium carbonate is added to a solution containing at least 5 eq. mercuric chloride to 1 eq. of ammonium salt, the ammonia is completely precipitated, even from very dilute solutions. The determination of the ammonia in the precipitate can be effected either by distilling the precipitate with sodic hydrate and sodium sulphide, and determining the ammonia in the distillate; or by dissolving the precipitate in hydrochloric acid and evaporating with platinic chloride and determining the weight of the ammonium platinum double salt; or by weighing the precipitate after drying it at 100°. The last method is only applicable, if the liquid contains less than 0.01 gm NH_3 in the liter. The precipitate seems to correspond to the formula $Hg_5N_2O_3H_2Cl_2$.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

June 3, 1879.

216,045.—*Restoring and preserving stone.* CH. O LUNDBERG.

Restoring and preserving stone by first washing it with an alkaline solution to destroy the acids which have been absorbed by the stone; then applying a mixture of lime-putty, hydraulic cement and water, and then applying a solution of an alkaline silicate.

216,117.—*Process of casting steel ingots.* W. A. SWEET.

To prevent piping in ingots, the molten metal while in the mould is covered with a highly heated substance, such as charcoal or molten slag, capable of protecting the metal from the outer air and permeable by the gases evolved in casting.

216,118.—*Apparatus for the production of gas for metallurgical and other purposes.* C. TESSIÉ DU MOTAY and E. J. JERZMANOWSKY.

Oxidizing and carbonizing gases are produced in separate generators and stored in separate holders, and supplied under the desired pressure and in regulated quantities, either together or separately to metallurgic or other furnaces, for producing different temperatures, and either carbonizing or oxidizing flames.

216,207.—*Compositions for applying colors.* A. E. MERY.

A compound consisting of glue, glycerine, water, white wax, ammonia and rosin, dissolved in ether, to be mixed with the coloring matter and to be used as a paint.

June 10, 1879.

216,290.—*Compounds for preventing the destruction or rotting of bags.* E. OSGOOD.

A compound of beeswax, tallow and tar is to be applied to bags in which certain fertilizers are to be transported.

216,414.—*Preserving compounds.* H. JANNASCH.

Brief: Equal parts of chloride of potassium, nitrate of soda and chemically pure boracic acid are separately dissolved in water. The chloride solution is heated to boiling, the nitrate solution is then added and boiled until clear, when the boracic acid solution is added, while stirring. It is finally evaporated to dryness.

216,474.—*Processes for manufacturing solid collodion.* V. TRIBOUILLET and L. A. DE BESAUCELE.

This "solid collodion" is a mixture of camphor and nitro-cellulose, which can be moulded like celluloid, and used for the manufacture of various articles. It is proposed to manufacture nitro-cellulose in closed glazed vessels.

216,483.—*Separating potash from ashes.* J. and R. H. WOODRUM.

The inventors pour boiling water on the red hot ashes and let it percolate.

June 17, 1879.

216,518.—*Processes of converting crude petroleum, without practically changing its volume, into a uniform, purified and deodorized oil, which may be distilled without the coming over of naphtha, etc.* H. F. HOWELL.

According to the inventor, this remarkable result is obtained by the treatment of the crude oil with chlorine gas.

216,519.—*Processes and apparatus for manufacturing illuminating gas.* R. M. HUNTER.

Hydrogen is produced by decomposing steam by heated spongy iron (from iron ore), and after addition of hydrocarbon vapors, is transformed into a fixed illuminating gas, by reheating in a separate retort.

216,547.—*Compounds for covering roofs and vessels and for other purposes.* J. WETTENDORFF.

4 parts of cement, 3 of unslaked powdered lime, 2 of powdered rosin mixed with clabber milk.

216,557.—*Apparatus for making extracts and distilling liquids.* MATYAS CZINER.

216,558.—*Bleaching oils and fats.* J. DAVIS.

The bleaching is effected by treating the oil first with a mixture of bichromate of potash and caustic soda dissolved in water, then adding sulphuric acid to the whole mixture and finally washing with water.

216,584.—*Processes and apparatus for manufacturing carbonic oxide.* C. TESSIÉ DU MOTAY and E. J. JERZMANOWSKY.

Carbonic oxide is produced from wood, turf or other carbonaceous refuse by incomplete combustion, and by passing the products of combustion through incandescent coal. The principal feature of the patent is the arrangement of apparatus.

216,589.—*Preserving wood.* W. WELLHOUSE and E. HAGEN.

Wood is treated with a solution of chloride of zinc and gelatine, and afterwards with a solution of tannin to close the pores.

216,596.—*Friction compounds for belts.* F. BROWN.

A compound of oil, beeswax, india-rubber and gum arabic to prevent the slipping of belts.

216,613.—*Manufacture of artificial fuel.* O. HASSEL.

Powdered peat or coal dust are mixed with sea-grass or sea-weed boiled to a jelly, the mixture pressed into blocks, dried and coated with pitch.

216,625.—*Inks for printing protective tints on commercial blanks.* E. MENDEL.

An ink composed of glycerine, starch, zinc-white, grape sugar or glucose and coloring matter.

June 24, 1879.

216,816.—*Methods of treating bones for glue-stock.* WM. ADAMSON.

Before the usual acid treatment, the bones are treated with hydro-carbons, in order to remove the fat.

216,850.—*Roofing paints or coverings.* J. R. HAZELET.

A number of oils and rosins dissolved in volatile hydro-carbons and mixed metallic paints.

216,910.—*Dephosphorizing iron.* S. G. THOMAS.

Claim 1 : In the dephosphorizing of iron, where highly basic slag is produced in the Bessemer or open hearth operations, the process of producing such slag, which consists in lining the converter or other vessel with calcareous or magnesian material, and adding to the molten metal therein basic material containing two-thirds of lime or lime and magnesia, and of a gross weight equal to about five times the weight of the silicon and phosphorus contained in the charge, the said basic material being divided and a part added before lapping, and the remainder after this has been blown, or the whole quantity added at once.

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